

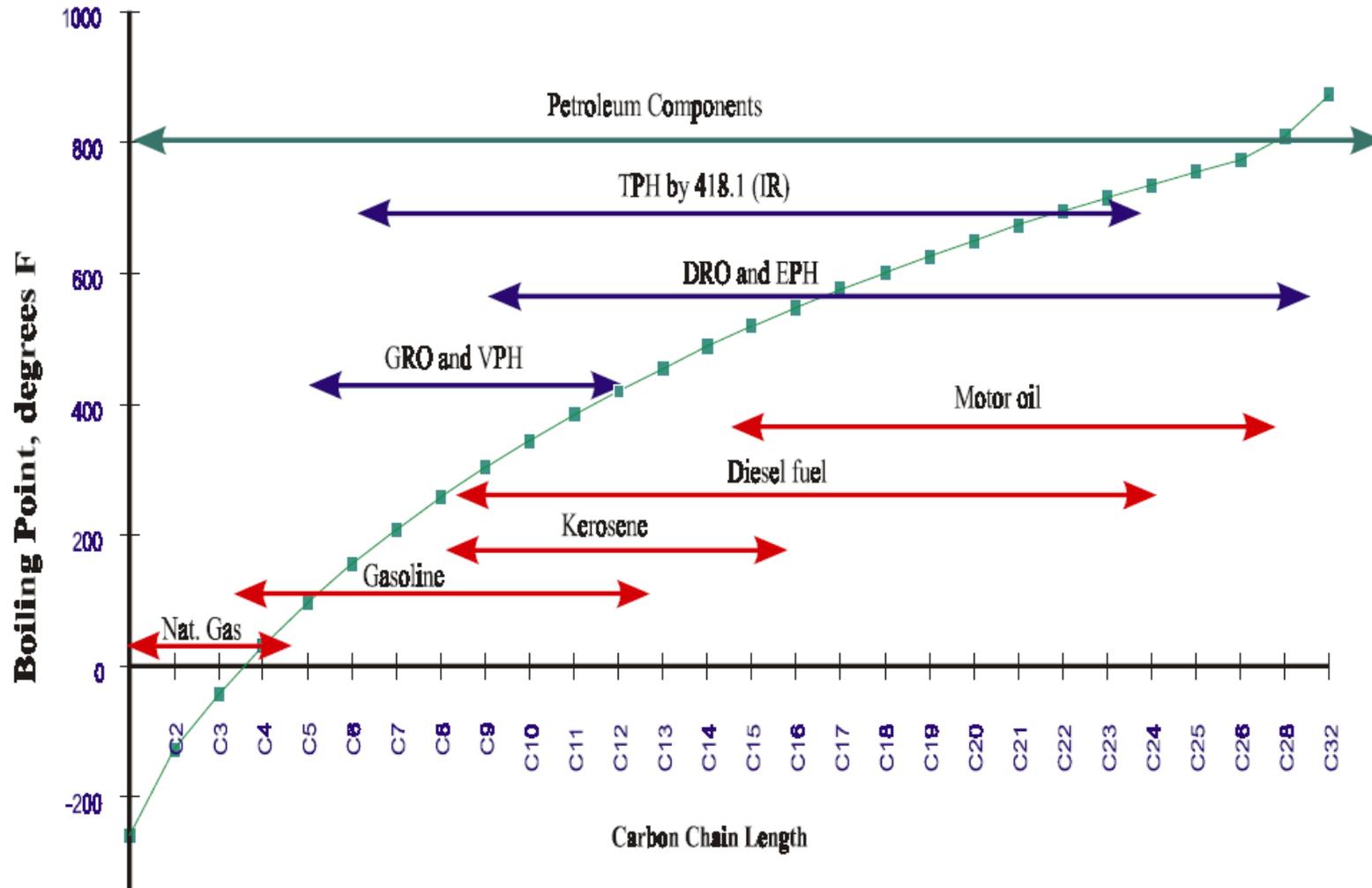
PETROLEUM HYDROCARBONS AND PETROLEUM HYDROCARBONS MEASUREMENTS

Approved Continuing Education Course, Massachusetts Department of
Environmental Protection, Board of Registration of Hazardous Waste Site
Cleanup Professionals: Course 1092, 4 credits, Copyright: May 1997

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Petroleum Products and Petroleum Hydrocarbons Measurements



General

This presentation provides an atlas of common petroleum hydrocarbon profiles and a description of common techniques used to quantify petroleum hydrocarbon contamination. The presentation stresses the importance of interpreting site-specific petroleum contamination beyond simple total petroleum hydrocarbons numbers using gas chromatographic component profiles.

This booklet represents the curriculum document for our petroleum hydrocarbons course which is approved for 4 technical credits by the Massachusetts Board of Registration of Hazardous Waste Site Cleanup Professionals (1092) .

Petroleum Hydrocarbons

Environmental contamination by petroleum hydrocarbons is the most common site contamination issue encountered by environmental professionals. The nature of petroleum hydrocarbon contamination is highly variable. Petroleum hydrocarbons themselves are diverse mixtures of chemical components. Site characterization as well as risk assessment is best accomplished with insight on site-specific contaminant compositions.

The components of petroleum and petroleum products number in the tens of thousands. They range in molecular weight from methane (16) to very large uncharacterized components with molecular weight in the thousands. The toxicity of the components varies immensely. Overall, the components of these mixtures have only two common properties: They are derived from petroleum and they contain hydrocarbon functional groups (C-H).

The more common functional categories of compounds found in petroleum products are n-alkanes, branched alkanes, cycloalkanes, and aromatic compounds. In certain mixtures there are other functional categories present (alkenes, mercaptans, porphorins, etc.) Added chemicals such as petroleum oxygenates (MBTE, et al.) are sometimes included.

In the environment, petroleum component mixtures are subject to weathering effects such as volatilization, biodegradation, partitioning into water, oxidation, and photodegradation. These effects change the distribution of components in a mixture and change the chemical composition of components as well.

The “Petroleum Products and Petroleum Hydrocarbons Measurements” chart on the previous page illustrates boiling point (actually, vapor pressure) distribution ranges for some petroleum products. The “X” axis is calibrated using normal alkane standards ranging from methane (C1) to dotricontane (C32). Volatility decreases to the right.

Also included on this chart are applicable ranges for certain analytical methods frequently used in testing petroleum hydrocarbons levels.

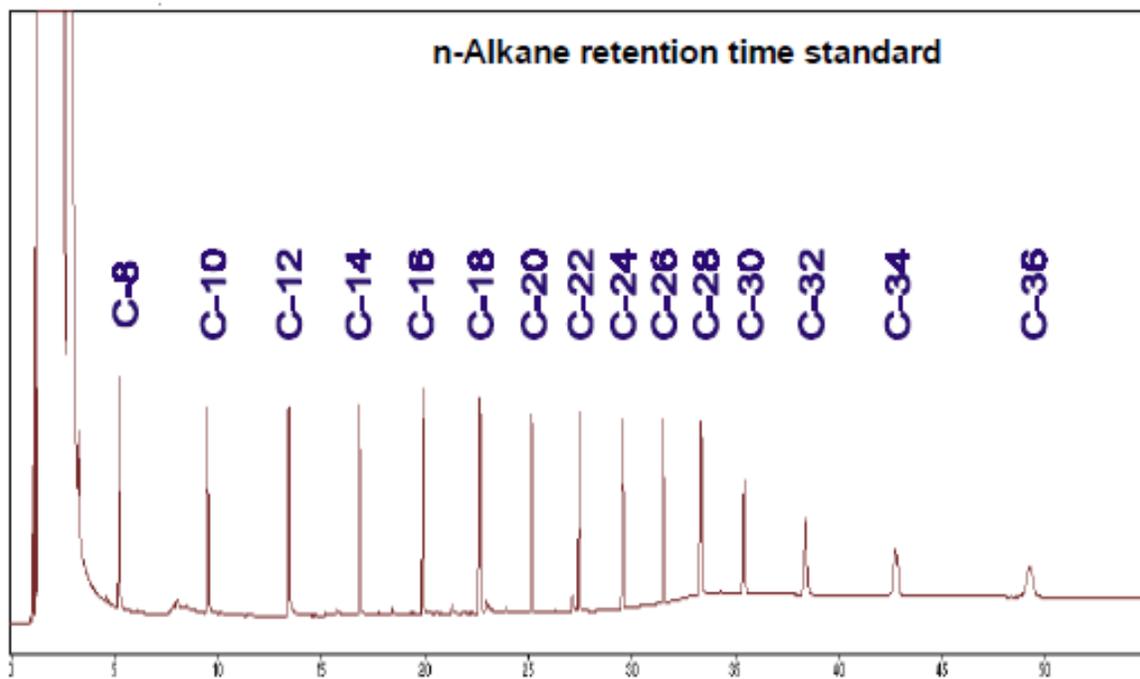
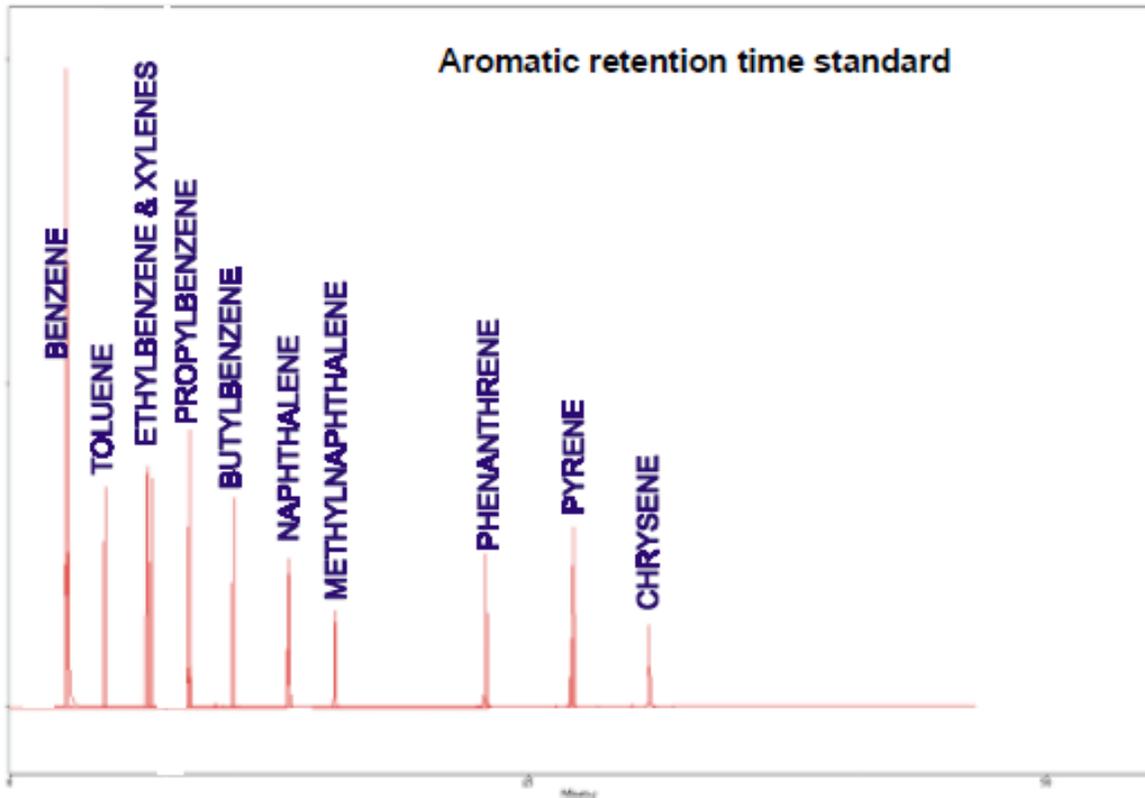
This presentation builds upon the general concepts in the chart using petroleum hydrocarbon fingerprints obtained using gas chromatography.

Gas Chromatographic Profiling of Petroleum Hydrocarbons

Gas chromatography is a technique for separating and detecting components of mixtures. In obtaining component profiles for petroleum hydrocarbons the gas chromatograph is configured to separate components based on component vapor pressures over a range extending from butane (n-C₄H₁₀) to dotricontane (n-C₃₂H₆₆). This window includes products from gasoline through paraffin wax.

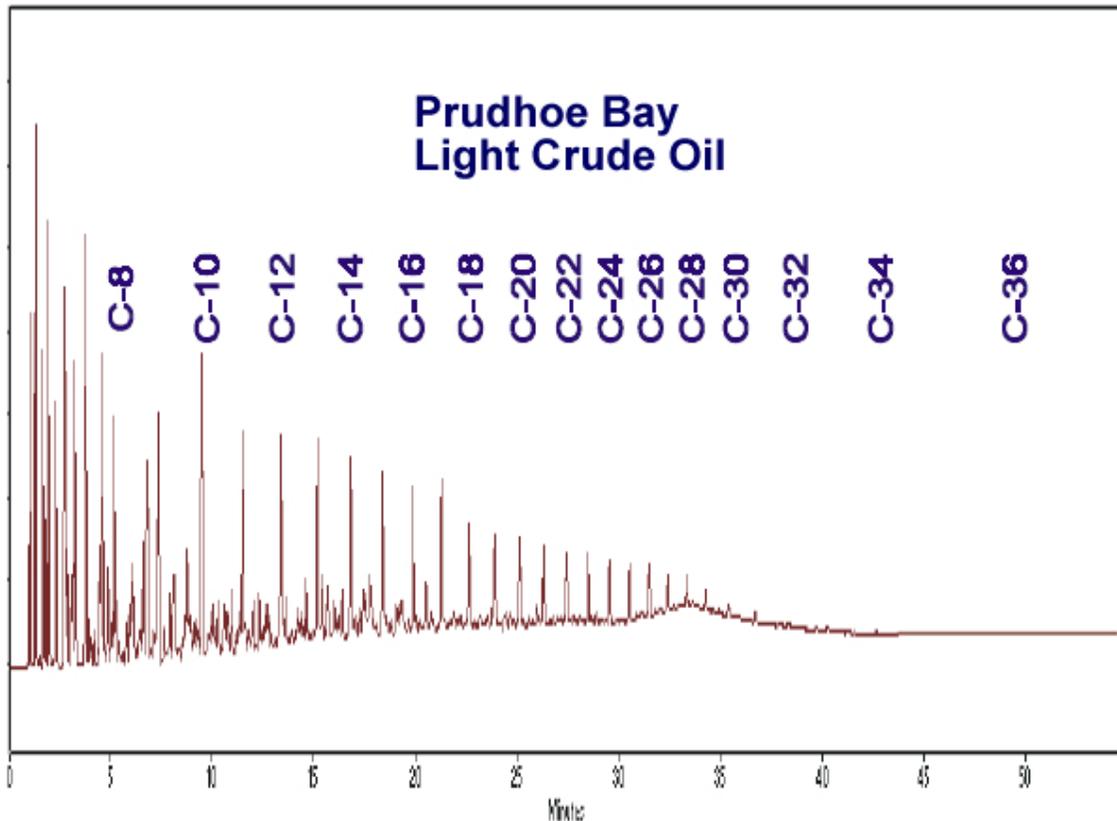
The "X" axis is calibrated using hydrocarbons of known vapor pressure. The "Y" axis is a component concentration axis. The peaks are individual compounds or mixes of compounds with the same volatility.

The conditions used to obtain the pictured retention time standard profiles were used for all chromatograms in this presentation unless otherwise noted. This enables direct comparison of profiles for different products, etc.



Crude Oil and Petroleum Product Production

Crude oil is the raw material used by refineries in manufacturing petroleum products. The composition of crude oil varies considerably from source to source. Some crudes, like the Prudhoe Bay Light Crude pictured, contain a considerable amount of low and medium weight hydrocarbons. Others are very heavy, tar-like materials. The refinery adapts its process to manufacture as much gasoline (the product with the highest commercial demand) as possible from a given crude. Diesel fuel/No. 2 heating oil is second in demand. Hundreds of other products are manufactured from crude oil including jet fuel/kerosene, lubricants, asphalt, coke, petrochemical feedstocks, LPG, etc.



Straight-run distillates

The fundamental refinery process is distillation of the crude into low-boiling, medium-boiling, high-boiling and residual fractions. These fractions are used directly in some cases and are called straight-run distillates. Heating fuel (No. 2) is usually a straight-run distillate.

Blended products

To maximize gasoline production, medium and high weight fractions are converted to low weight materials in a process called cracking/reforming. The resulting "reformate" is blended with low weight straight-run distillate. Additives are included such as gasoline oxygenates to improve performance. Straight-run distillates are also blended to achieve specifications and improve yields for various fuel oils.

Further refined products

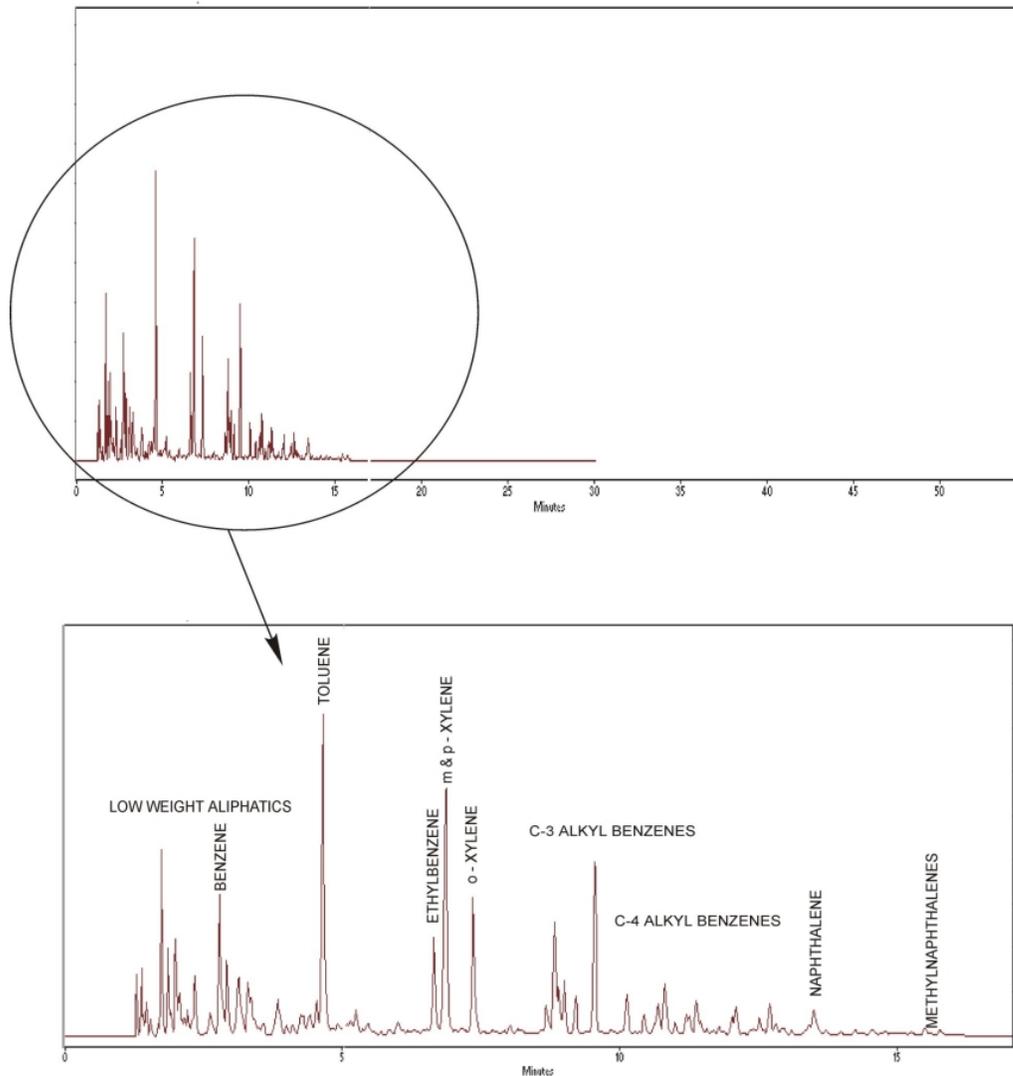
Additional processing yields highly refined products like lubricating oils, waxes, chemical feedstocks, etc. Diesel fuels are essentially No. 2 fuels with added processing to remove sulfur and waxes.

Gasoline

Gasoline is a low-weight, high-volatility blended product. Benzene and alkyl-substituted benzenes are predominant components. Addition of volatile oxygenated organics such as t-butyl methyl ether improve combustion efficiency of the product. These oxygenates are more water soluble than other components in the blend and migrate more rapidly in the environment.

Gasolines from different sources and of varying grades have very similar component profiles.

Gasoline



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Overhead 4

Diesel Fuel

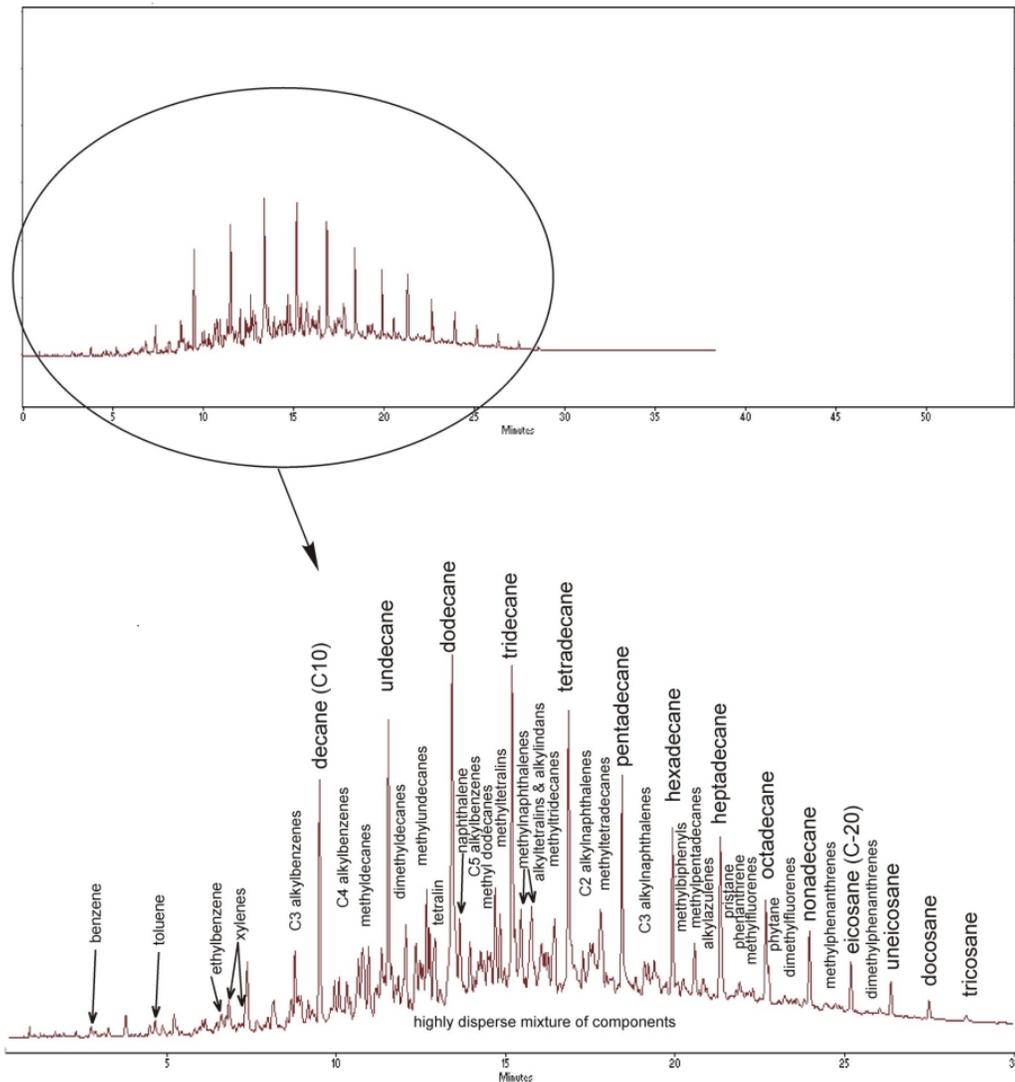
Diesel fuel and No. 2 heating oil are usually straight-run distillates with the same gross component profile. They have the same manufacturing specification except diesel fuel is lower in sulfur (and sometimes wax) content. The predominant peaks are n-alkanes. The majority of the remaining components are alkyl-substituted aromatics and branched and cyclic aliphatics.

No. 4, No. 5, and No. 6 fuel oils also have similar component profiles but the distributions are shifted to the higher boiling component end of the range. Sometimes these heavier fuels are straight-run distillates, but frequently they are blends of distillates with residuum (the nonvolatile bottoms of the distillation process) and cracked residuum. "Bunker C" is primarily a residuum based product.

Diesel fuel profiles are nearly identical from source to source.

#2 Fuel Oil

Equivalent Profile for Diesel Fuel



Environmental Degradation

Weathering

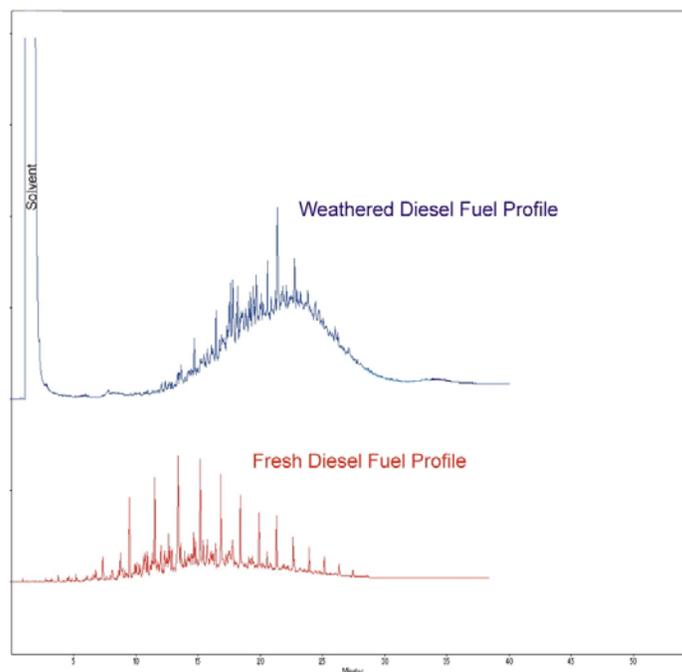
In the environment, volatilization, biodegradation, partitioning into water, and photodegradation alter the component profile of diesel fuel. N-alkanes are considerably more biodegradable than branched alkanes and alkyl aromatics, and their peaks in the profile quickly attenuate. Lower boiling components are more biodegradable, more water-soluble, and more volatile than higher weight components and are removed from the mixture sooner.

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.

Note the exaggerated hump in the weathered diesel profile. This hump is present in the fresh profile but becomes a predominant feature as the n-alkanes are selectively removed from the mixture. The hump is caused by the superimposition of hundreds (perhaps thousands) of component peaks with low individual concentrations and overlapping volatilities. The mass of the hump material is believed to increase as degradation proceeds because stochastic environmental processes tend to produce a diverse set of metabolites from the original components.

All petroleum hydrocarbon mixtures undergo similar degradation in the environment. Even after considerable weathering, the profiles for the resultant residuals have a conspicuous “signature” revealing their petroleum product precursor.

Environmental Degradation

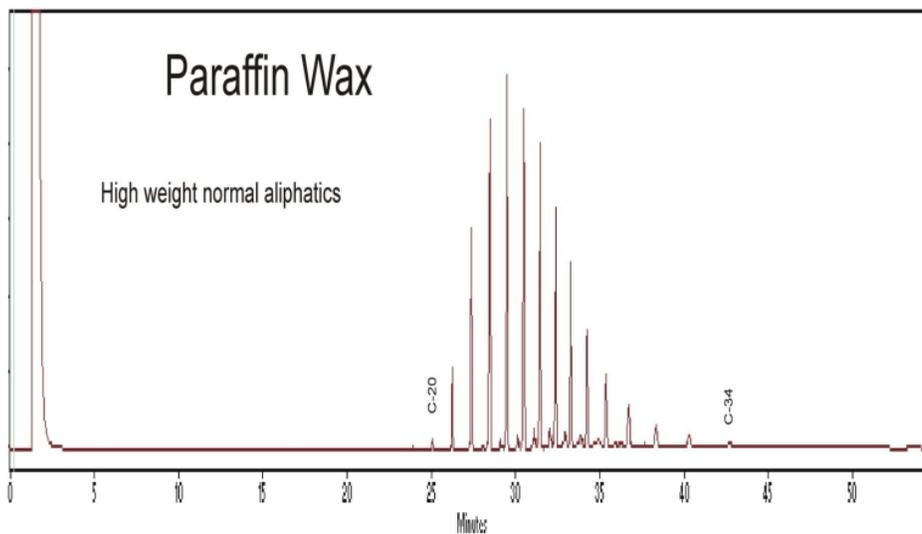
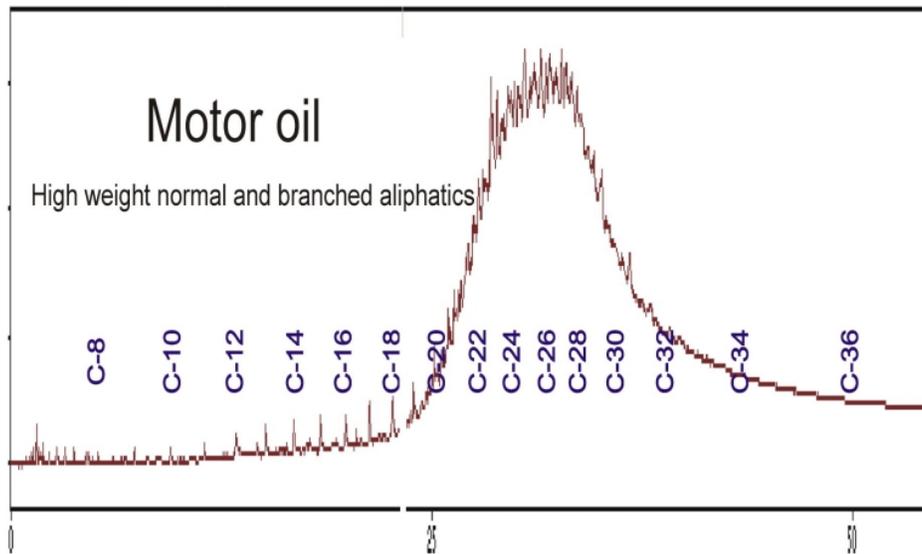


Component Profiles for Common Petroleum Products

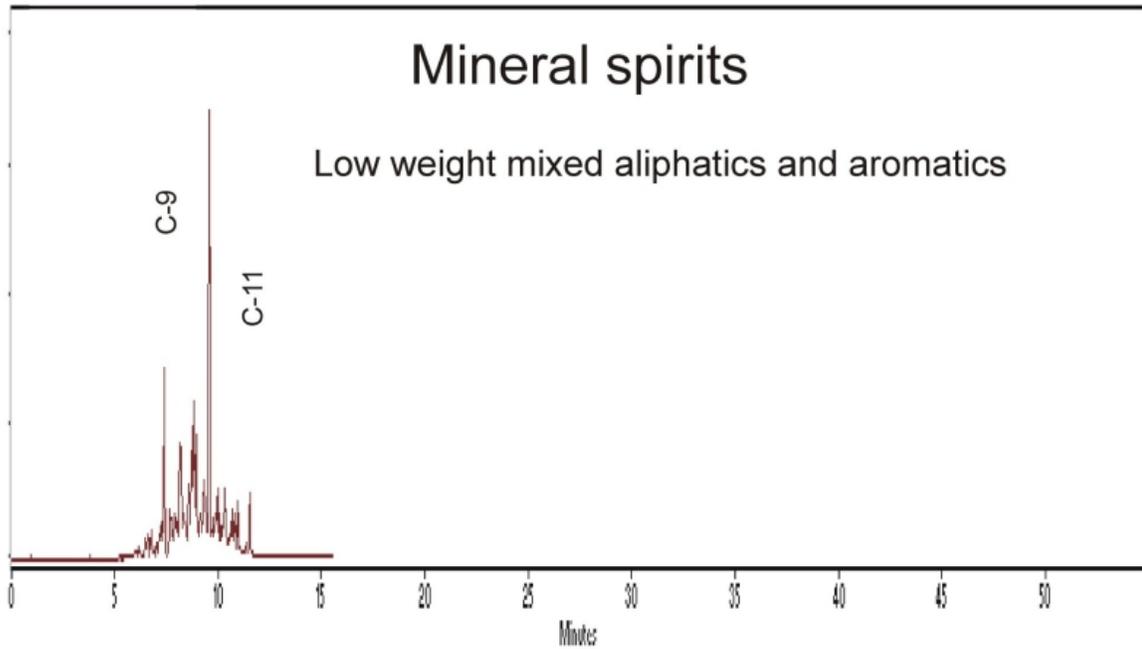
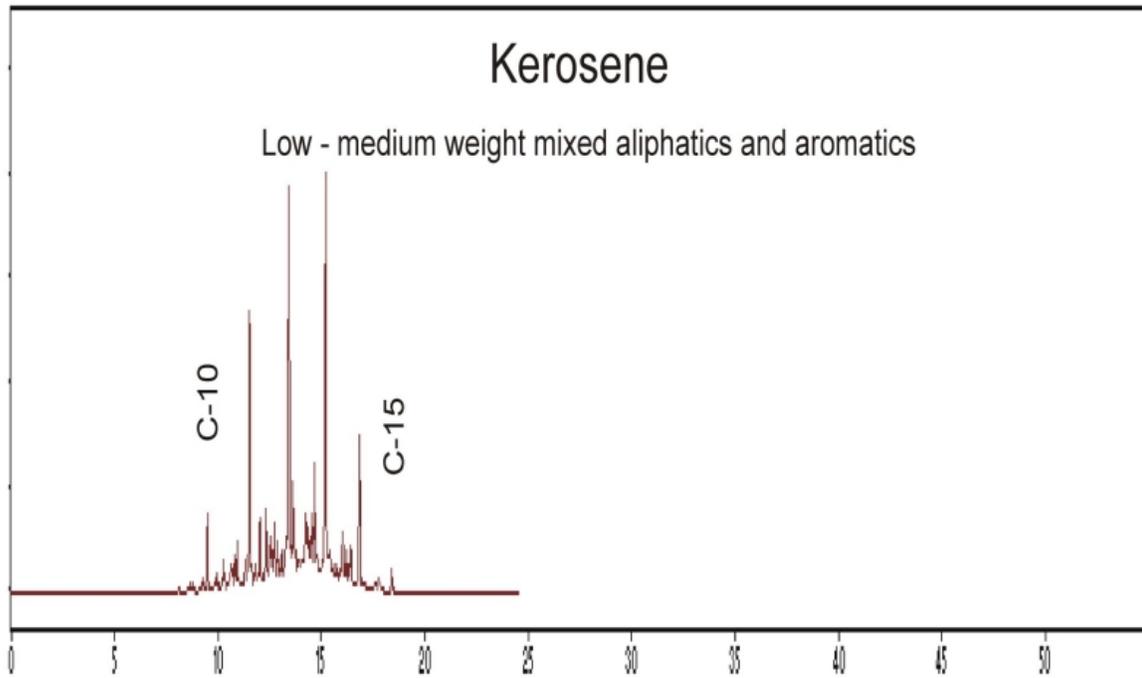
Other Petroleum Hydrocarbons

- Motor oil is a refined formulation of mostly high-weight branched and cyclic alkanes. Additives include rust inhibitors, viscosity modifiers, detergents, and synthetic lubricants.
- Paraffin wax is almost entirely n-alkanes.
- Mineral spirits is primarily low weight mixed aliphatics and aromatics
- Kerosene (No. 1 fuel oil) and mineral spirits are straight-run distillates.

Component Profiles for Common Petroleum Products



Component Profiles for Common Petroleum Products



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Non-Petroleum Hydrocarbon Mixtures

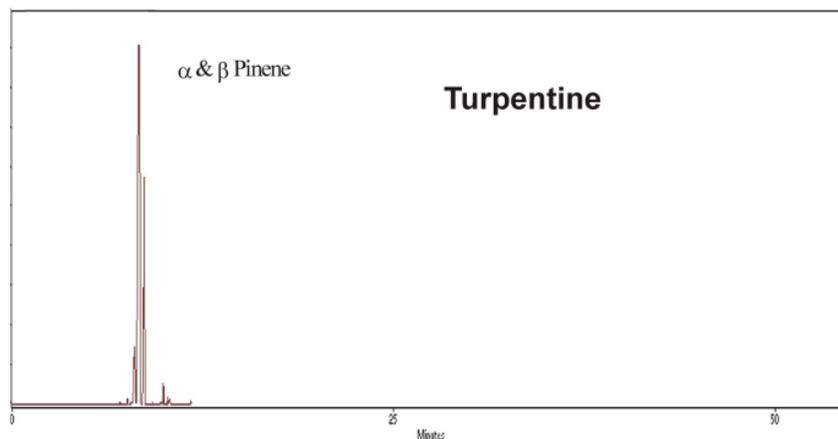
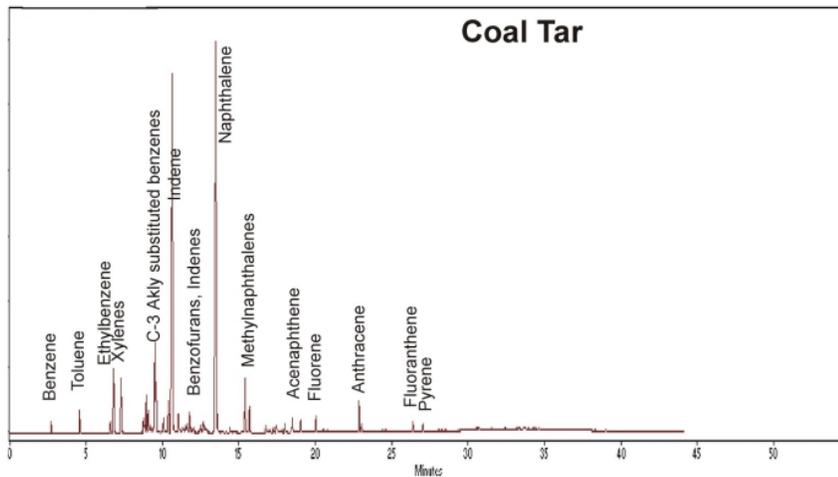
Non-petroleum derived organic compounds or mixtures of compounds within the appropriate vapor pressure range will give a chromatographic response. Coal tar creosote is one example. This medium boiling range material is easily distinguished from petroleum hydrocarbon products by its profile and its predominately aromatic composition.

In certain foreign countries (e.g., South Africa) where petroleum is scarce but coal is common, diesel fuels are produced from coal tar.

Turpentine is a natural occurring mixture of pinenes.

These non-petroleum mixtures as well as hundreds of other naturally occurring and synthetic compounds and compound mixtures give positive results by all petroleum hydrocarbon measurement techniques. Although Total Petroleum Hydrocarbon (TPH) numbers have their use, a chromatographic profile is indispensable in understanding the nature of the contaminant being measured.

Non-Petroleum Hydrocarbon Mixtures



Measuring Petroleum Hydrocarbons

Infrared Spectrometric Methods for TPH Measurements

An infrared spectrometer is a device which measures a sample's transparency to the range of frequencies in the infrared band of the electromagnetic spectrum. The instrument provides a plot of radiation absorbed vs radiation frequency called an infrared spectrum. A sample infrared spectrum is presented below.

The character of a sample's infrared spectrum (the frequencies at which radiation is absorbed and the intensities of those absorbances) is a function of the types and abundances of chemical bonds present in the sample. For example, the C=O in ethers produces an absorbance at ca. 1740 cm^{-1} and the C-H bond in hydrocarbons produces an absorbance ca. 3000 cm^{-1} . Infrared analysis of TPH uses the absorbance at 3000 cm^{-1} to measure the presence of hydrocarbons, then assumes they are all petroleum based materials. The method involves:

Extracting the sample with a solvent that has no C-H functionality of its own. The solvent chosen is trichlorotrifluoroethane (Freon^(TM)).

Removing polar (presumably non-petroleum components from the extract with an absorbent.

Measuring the extract's absorbance at 3000 cm^{-1} and calculating the hydrocarbon concentration using a calibration graph prepared from arbitrary hydrocarbon standards.

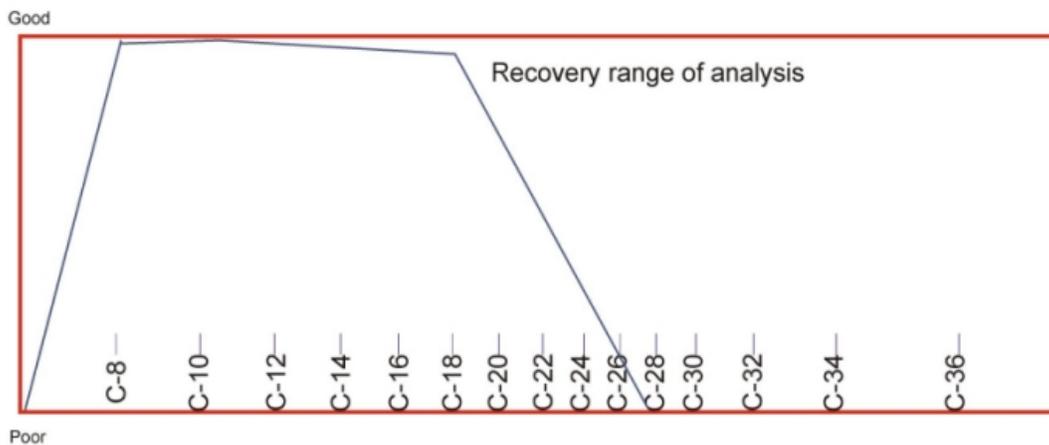
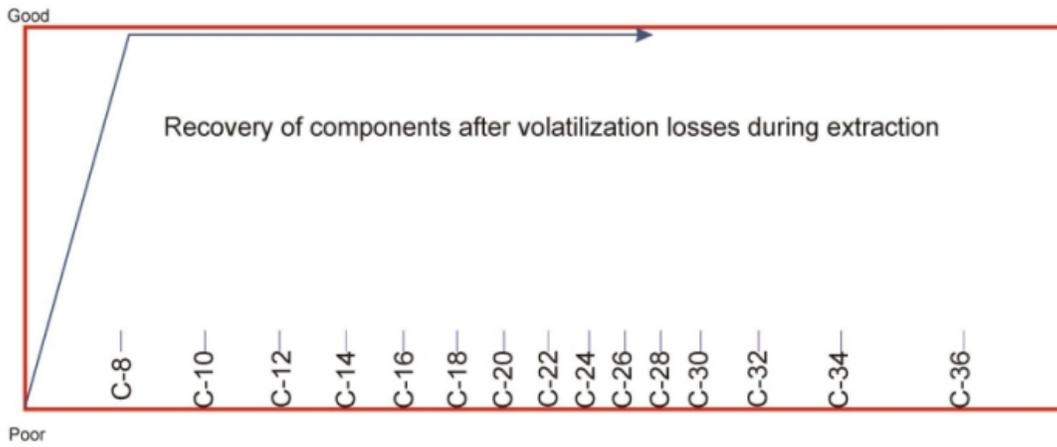
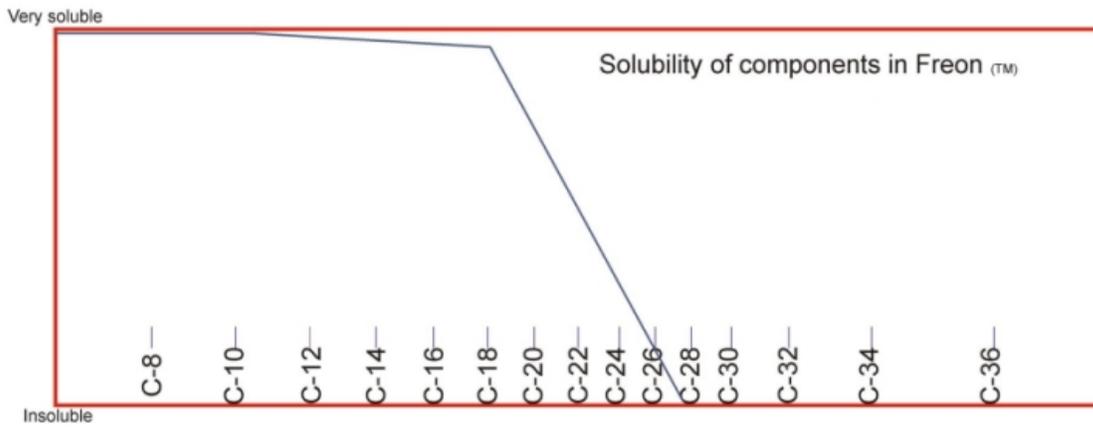
There are limitations to this method:

Only a concentration value results from the analysis - a number related to the sample extract's opacity at the invisible frequency of 3000 cm^{-1} . No insight as to what is being measured is provided. Volatile components are lost in extraction.

Weathered products and products with high weight components have limited solubility in Freon^(TM). Freon^(TM) is a chlorofluorocarbon and is an ozone depleting chemical with EPA use restriction.

Do not use this method to establish the presence of hydrocarbons or to evaluate risk. This method may be used effectively to establish boundaries of remediation when excavating soils known to be contaminated by petroleum. It should not be used to evaluate extent of remediation by other processes such as bioremediation.

Infrared Spectrometric Methods for TPH Measurements



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Diesel Range Organics (DRO) and Gasoline Range Organics (GRO)

Diesel Range Organics (DRO) and Gasoline Range Organics (GRO) are two gas chromatographic methods for measuring hydrocarbon contamination. These methods were developed and published by the American Petroleum Institute in the mid-1980s. They both provide numerical results for their corresponding ranges of hydrocarbons using appropriate petroleum hydrocarbons as standards.

The GRO analysis utilizes a purge & trap sample introduction technique for transferring components from the sample to the GC, and low weight, high volatility components are well recovered. Use of this purge & trap technique is described in SW-846, Method 5030. The analysis of volatile, non-halogenated organic compounds by FID/GC is described in SW-846, Method 8015. EPA does not have an approved method for the analysis of GRO, but this technique is often called EPA 5030/8015 for reasons stated above.

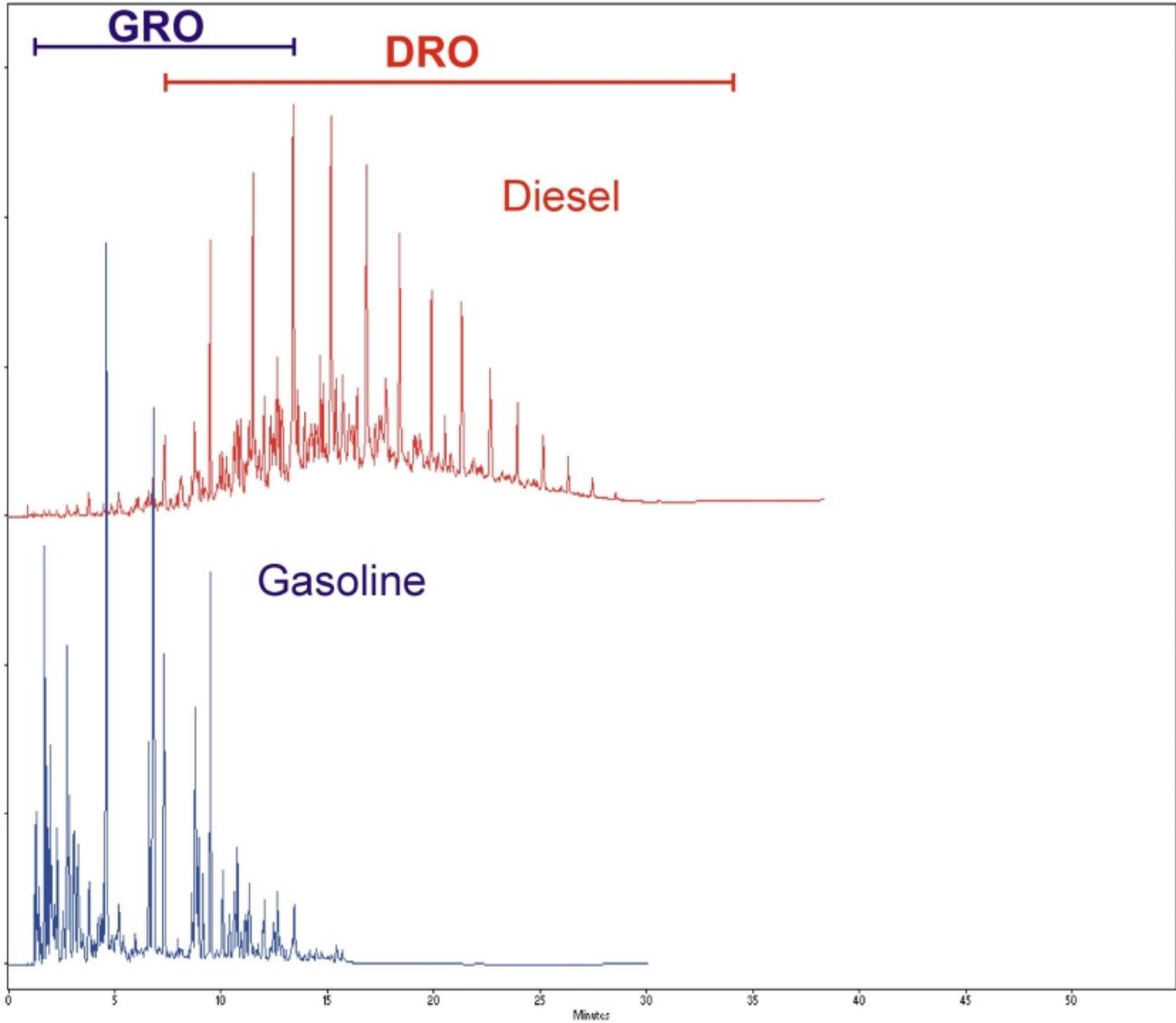
The DRO analysis utilizes an ultrasonic extraction in sample preparation. This extraction is discussed in EPA SW-846, Method 3550. The analysis of pre-extracted, non-halogenated organic compounds (specifically polynuclear aromatic hydrocarbons) by FID/GC is described in SW-846, Method 8100. The analysis of DRO does not have an EPA approved procedure either but it is often called EPA 3550/8100.

Many states have their own procedures for GRO and DRO.

As the chart indicates, the DRO and GRO ranges overlap. Caution is recommended in adding the GRO and DRO values to obtain a total. For many products and contaminants, certain components are counted twice. (The mineral spirits profile is entirely within both the GRO and DRO ranges!)

Both methods provide usable chromatographic profiles for interpreting the nature of site-specific contamination. Use these methods in scouting for petroleum hydrocarbon contamination during site assessments and monitoring of remediation processes.

Diesel Range Organics (DRO) and Gasoline Range Organics (GRO)



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MADEP EPH Profiles for the Method Standard

Extractable Petroleum Hydrocarbons (EPH)

Toxicity and risk vary considerably among petroleum contaminants. In general, aromatic compounds are more toxic than aliphatic compounds. Low weight contaminants are more toxic (more bioavailable is a better term) than high weight components. Providing a risk-indexed number for petroleum hydrocarbon contamination levels is the objective of both the MADEP EPH and VPH methods.

The EPH method uses a post-extraction liquid chromatographic preparation step to split the extract into aromatic and aliphatic fractions. The profiles in the view graph show how effectively this is accomplished. Once separated, chromatograms are obtained for both fractions. The chromatographic profile for the aliphatic fraction is integrated over two ranges for two results: C₉ to C₁₈ aliphatics and C₁₉ to C₃₆ aliphatics.

The aromatic fraction's chromatogram is used to quantify individual target polynuclear aromatic hydrocarbons. The entire profile is integrated with the exception of the target polynuclear aromatic hydrocarbons to obtain a C₁₁ to C₂₂ aromatics result.

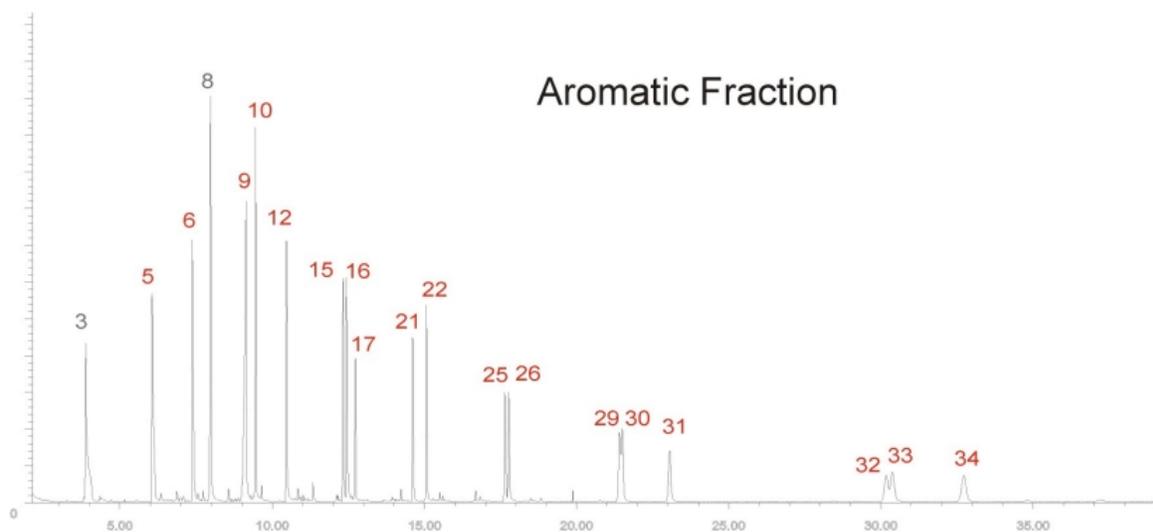
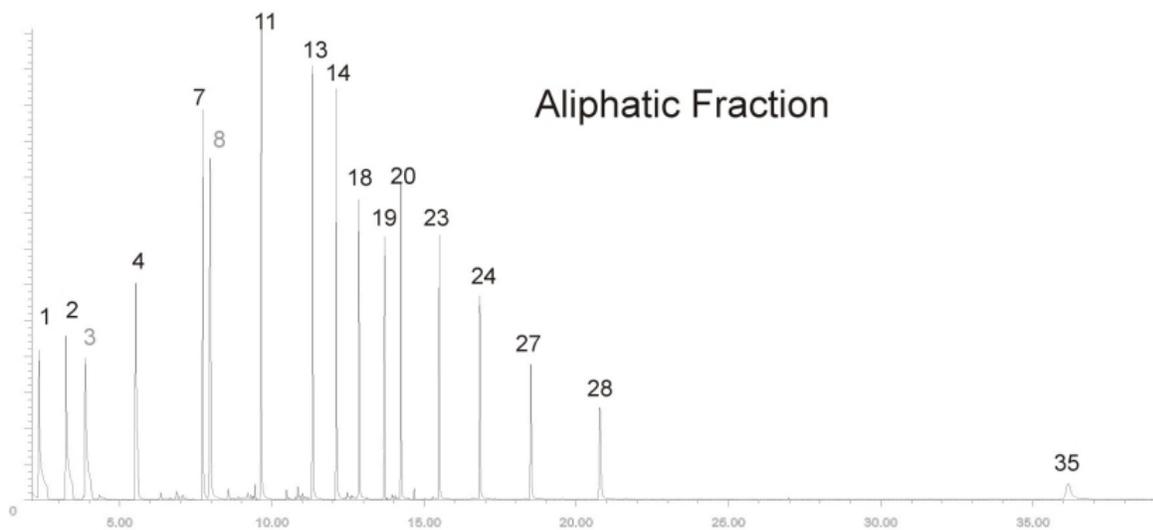
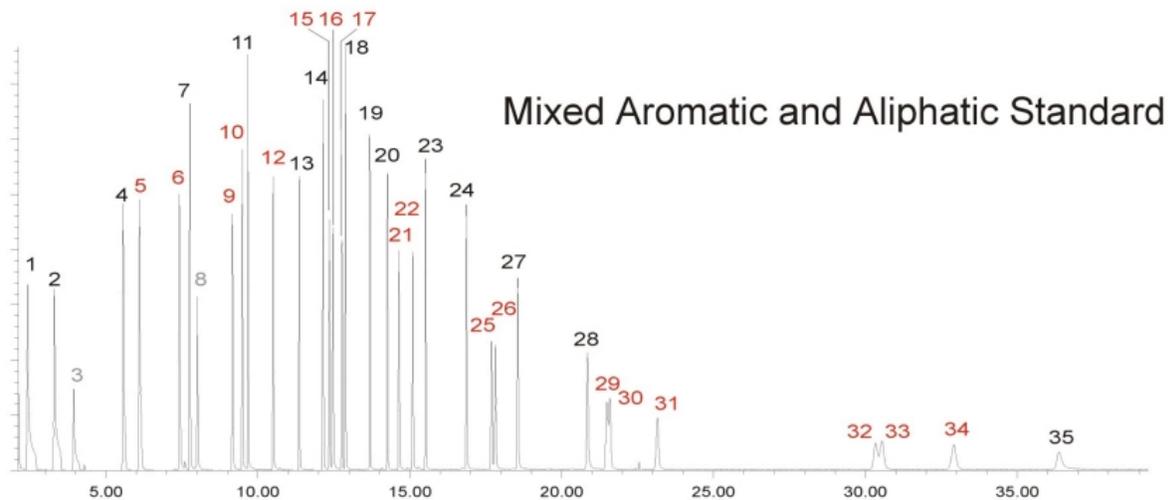
A table of individual, targeted polynuclear aromatic hydrocarbons must also be presented with the results to conform with the MADEP SOP.

Use this method to perform risk assessment for sites where petroleum hydrocarbon contamination has been previously established.

Table of Components for the method standards

Peak #	Compound	Peak #	Compound
1	Nonane	19	1-Chloro-octadecane
2	Decane	20	Docosane
3	1,4-Dichlorobenzene-d4	21	Fluoranthene
4	Dodecane	22	Pyrene
5	Naphthalene	23	Tetracosane
6	2-Methylnaphthalene	24	Hexacosane
7	Tetradecane	25	Benzo(a)anthracene
8	Fluorobiphenyl	26	Chrysene
9	Acenaphthylene	27	Octacosane
10	Acenaphthene	28	Triacontane
11	Hexadecane	29	Benzo(b)fluoranthene
12	Fluorene	30	Benzo(k)fluoranthene
13	Octadecane	31	Benzo(a)pyrene
14	Nonadecane	32	Dibenz(a,h)anthracene
15	Phenanthrene	33	Indeno(1,2,3-cd)pyrene
16	Anthracene	34	Benzo(g,h,i)perylene
17	o-Terphenyl	35	Hextriacontane
18	Eicosane		

MADEP EPH Profiles for the Method Standard



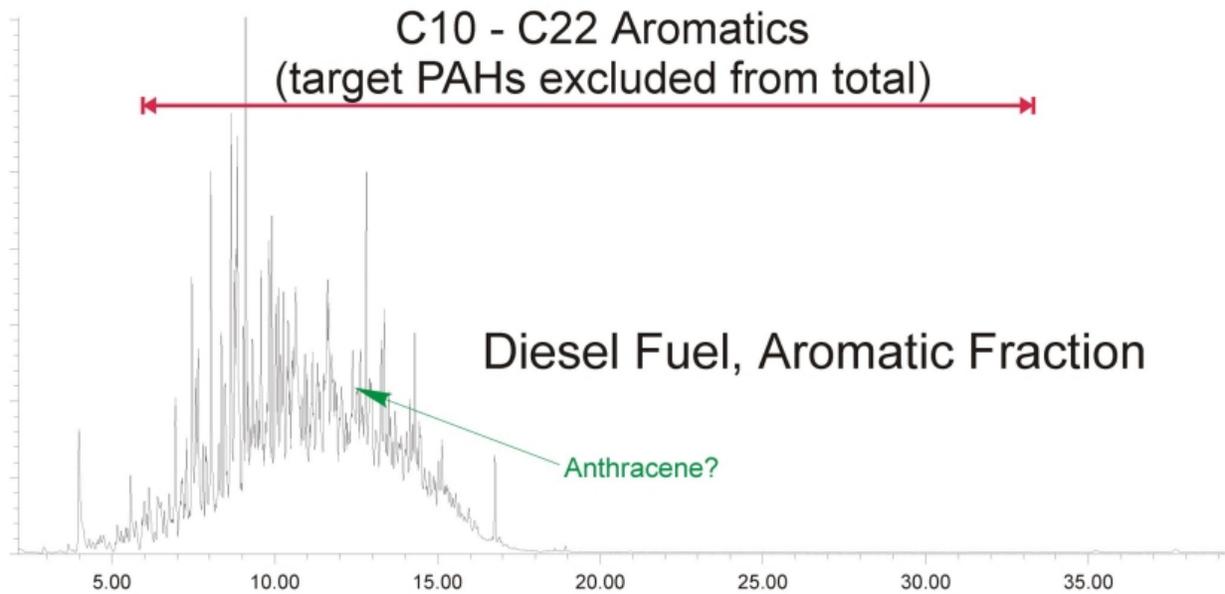
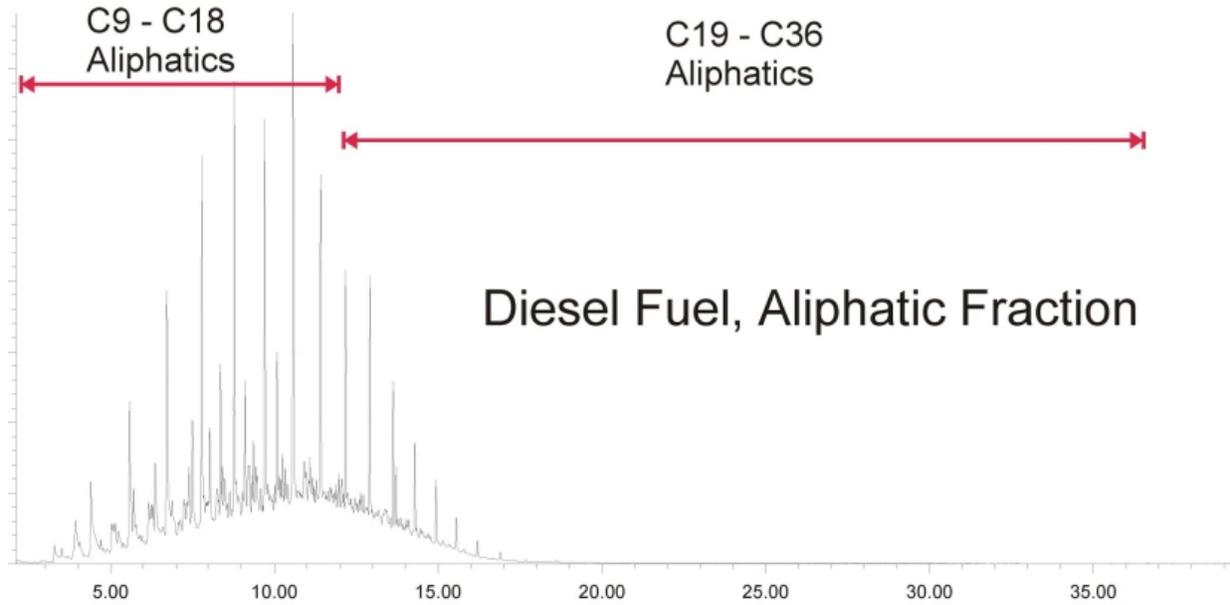
EPH Profiles for a Diesel Sample

In the following chart, a real-world sample (fresh diesel fuel) is subjected to the EPH analysis. Note that the profile - like most real-world profiles - is riddled with peaks. When using a non-specific GC detector like an FID, performing analysis for individual polynuclear aromatic hydrocarbons is quite risky. A peak eluting within a compound's retention time window may not be the compound of interest. In fact, it is hard to imagine a peak not occurring at just about any retention time between 5 and 15 minutes in the pictured example. Even if a peak's identity were known, where should the baseline of integration be drawn? To get reliable polynuclear aromatic hydrocarbons results, insist on analysis by GC/MS. The MADEP SOP provides for this improvement.

The congestion of components in FID profiles also causes surrogate integration problems with this method. Poor surrogate recoveries do not necessarily indicate poor analysis with this - or any other - conventional detector technique.

(The profiles in the illustration are obtained using conditions optimized for this separation and cannot be compared to other profiles in the presentation.)

MADEP EPH Profiles for a Diesel Fuel Sample



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Volatile Petroleum Hydrocarbons (VPH)

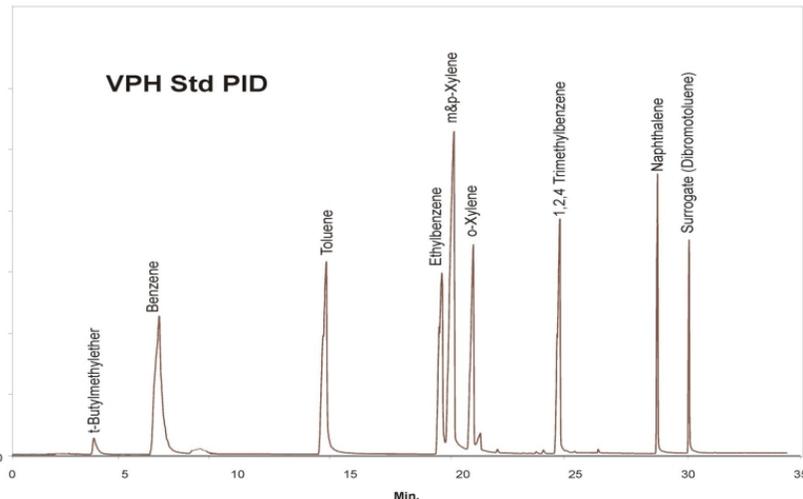
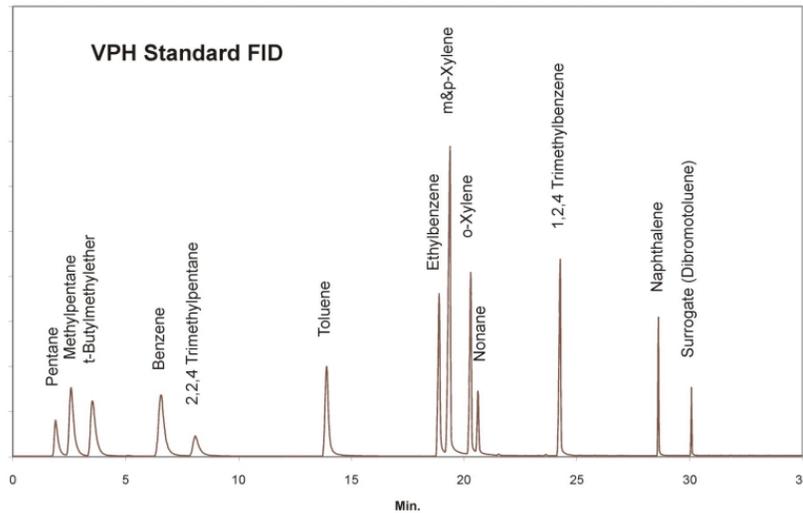
The VPH method uses a purge & trap for GC sample introduction. Chromatograms are obtained using two detectors, and FID and a PID. The PID is non-selective for alkanes and the chromatogram is considered to be primarily an aromatic profile. The FID gives a total hydrocarbon profile.

The chromatographic profile for the PID is used to quantify individual target aromatic hydrocarbons as well as C₉ to C₁₀ aromatics. The FID chromatogram is integrated over two ranges to obtain C₅ to C₈ aliphatics and C₉ to C₁₂ aliphatics. Target aromatics are subtracted from the ranges to prevent considering these compounds twice.

A table of target analytes (BTEX, Naphthalene, MTBE) must also be presented with the results to conform with the MADEP SOP.

Again, use this method to perform risk assessment for sites where petroleum hydrocarbon contamination has been previously established.

MADEP VPH Profiles for the Method Standard



VPH Profiles for a Gasoline Sample

In this chart, a real-world sample (fresh gasoline) is subjected to the VPH analysis.

The range for the C₉ to C₁₀ aromatics analysis begins - as specified in the method - at 1,2,4-trimethylbenzene. Certain C₉ aromatics may not be included in this range.

MADEP VPH Profiles for a Gasoline Sample

