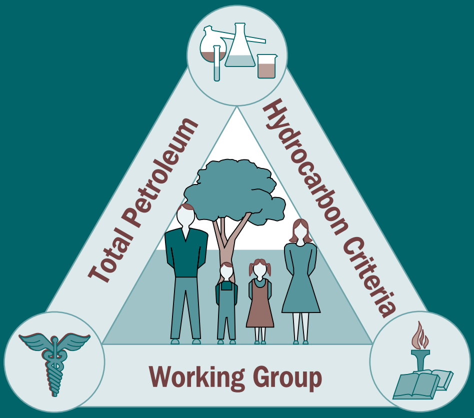
Total Petroleum Hydrocarbon Criteria Working Group Series

Volume 1

Analysis of Petroleum Hydrocarbons in Environmental Media



Analysis of Petroleum Hydrocarbons in Environmental Media

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Analysis of Petroleum Hydrocarbons in Environmental Media

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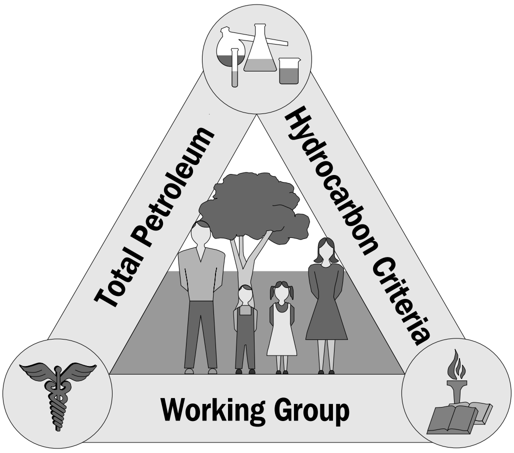

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A portion of the proceeds from the sale of this book will be donated to the Plant-a-Tree Program, a reforestation program managed by the U.S. Forest Service.

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PREFACE

This document is the first in a series from the Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG, or “Working Group”). The Working Group convened in 1993 to address the large disparity among cleanup requirements being used by states at sites contaminated with hydrocarbon materials such as fuels, lubricating oils and crude oils. These requirements usually focus on total petroleum hydrocarbon (TPH), with numerical standards ranging from tens to tens of thousands of milligrams of TPH per kilogram of soil. Recognizing that these standards are not based on a scientific assessment of human health risk, Working Group members established the following goal for their effort:

> *To develop scientifically defensible information for establishing soil cleanup levels that are protective of human health at petroleum contaminated sites.*

The Working Group is guided by a steering committee consisting of representatives from industry, government, and academia. Some of the active participants among the more than 400 involved include the Gas Research Institute, several major petroleum companies including Chevron, Exxon, British Petroleum and Shell, the American Petroleum Institute, the Association of American Railroads, several state governments (Washington, Texas, Colorado, Hawaii, Louisiana, New Mexico, Massachusetts), the U.S. Environmental Protection Agency, the Department of Defense, the University of Massachusetts, and private consulting firms including EA Engineering, Science & Technology and Menzie-Cura & Associates, Inc.

The Working Group compiled their data collection and analytical efforts into five volumes:

Volume 1. *Analysis of Petroleum Hydrocarbons in Environmental Media* (this volume) discusses and critiques analytical methods for quantifying TPH, petroleum mixtures and individual petroleum constituents in soil and water samples. It is designed to be a reference tool for the nonchemist, describing what information analytical methods can provide for risk assessment.

Volume 2. *Composition of Petroleum Mixtures* (in press) provides the best available composition information for a variety of petroleum products.

Volume 3. *Selection of Representative Total Petroleum Hydrocarbon (TPH) Fractions Based on Fate and Transport Considerations* (1997, Amherst Scientific Publishers) defines fractions of TPH expected to behave similarly in the environment. Identification of these fractions simplifies analysis of environmental samples, fate and transport modeling, and risk assessment efforts at petroleum contaminated sites.

Volume 4. *Development of Fraction-Specific Reference Doses (RfDs) and Reference Concentrations (RfCs) for Total Petroleum Hydrocarbons (TPH)* (1997, Amherst Scientific Publishers) provides the technical basis for the development of TPH fraction-specific RfDs and RfCs for use in the hazard assessment step of the Working Group's risk-based approach to establishing soil cleanup levels at petroleum contaminated sites.

Volume 5. *Human Health Risk-Based Evaluation Of Petroleum Contaminated Sites: Implementation Of The Working Group Approach.*(in press). This document integrates the findings of Volumes 1 through 4 into a risk-based framework for development of cleanup goals at petroleum contaminated sites. It includes descriptions of demonstration sites where the Working Group approach has been used successfully.

Amherst Scientific Publishers will publish these volumes in 1997 and 1998. In addition to these volumes, results of projects where use of the Working Group approach has been demonstrated (demonstration sites) and a concise technical summary document are now or will soon be available on the U.S. Air Force Toxicology Division web site (http://voyager.wpafb.af.mil). At this web site, Working Group publications may be downloaded from the "recent publications" icon. Additional Working Group resources will be added to this web site as they become available.

We hope you find these documents to be useful in your effort to evaluate and determine acceptable risk-based cleanup criteria at petroleum contaminated sites.

Wade H. Weisman
Chairman, TPH Criteria Working Group

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1. PURPOSE

The chemical composition of petroleum products is complex and may change over time following release into the environment. These factors make it difficult to select the most appropriate analytical methods for evaluating environmental samples. The Total Petroleum Hydrocarbon Criteria Working Group (the "Working Group") prepared this volume to assist site managers, risk assessors, regulators and others who may not have expertise in analytical chemistry in understanding the complexities of petroleum hydrocarbon characterization. This volume describes petroleum analytical methods and what they can and cannot tell you about environmental media (e.g., soil, groundwater, and surface water) at petroleum contaminated sites. The information provided in this volume will help the reader to accurately interpret results from petroleum analytical methods. This volume is not meant to be a comprehensive text on analytical methods and does not recommend or mandate any particular method. The goal of the Working Group is to provide the technical information needed by regulators, risk assessors, and site managers to implement health risk-based decisions at petroleum contaminated sites.

2. INTRODUCTION

There are a significant number of petroleum hydrocarbon impacted sites across the United States resulting from a wide range of past industrial, military, and petroleum production, and distribution practices. Difficulties in evaluating and remediating these sites arise from the complexity of the regulatory, scientific, and economic issues regarding impacted soil and water. Most investigations involving petroleum hydrocarbons are regulated by the states with different requirements in methodologies, action levels, and cleanup criteria. The chemical composition of petroleum products is complex and varied and changes over time and distance when released to the environment. These factors make it difficult to select the most appropriate analytical test methods for evaluating environmental samples and to accurately interpret and use the data.

The Working Group developed this volume to provide summary information about analytical techniques and methods for total petroleum hydrocarbons (TPH), petroleum by chemical class and boiling point ranges, and individual petroleum constituents. Newer fraction-based analytical approaches also are discussed. Discussion centers on analytical methods for soil, sediment, and water because most published methods measure TPH in these media. However, much of the discussion in this volume is relevant to other environmental media, such as air. Analytical methods for media such as sediment and air are often modified versions of established methods for soil and water.

This volume is organized into the following principal sections:

Section 3: Overview of TPH

This section provides an overview of the historical measurement and use of TPH data.

Section 4: Understanding The Petroleum Analytical Process: From Sample Collection To Measurement
This section provides a general overview of the analytical process characteristics that are common to most methods for quantifying TPH, individual petroleum constituents, and petroleum fractions.

Section 5: Total Petroleum Hydrocarbon (TPH) Measurement: Detailed Review Of Selected Analytical Methods
This section describes analytical methods for TPH that are based on four main analytical techniques: gas chromatography, infrared spectrometry, gravimetry, and immunoassay measurements.

Section 6: Petroleum Group Type Measurement: Detailed Review Of Selected Analytical Methods
This section describes analytical methods for petroleum groups that are based on two main analytical techniques: thin layer chromatography and immunoassay measurements. Petroleum groups include different categories of hydrocarbons such as saturates, aromatics, and polars/resins.

Section 7: Individual Petroleum Constituent Measurement: Detailed Review of Selected Analytical Methods
This section describes analytical methods for individual petroleum constituents that are based on four main analytical techniques: gas chromatography with photoionization detection, gas chromatography with flame ionization detection, high performance liquid chromatography, and gas chromatography with mass spectrometry detection. Individual petroleum constituents often include benzene, carcinogenic polycyclic aromatic hydrocarbons, and other compounds commonly associated with petroleum.

Section 8: Evolving Methods For Petroleum Hydrocarbon Fractions
This section provides an introduction to several newer analytical methods for quantifying petroleum fractions rather than TPH, groups or individual constituents. It explains why such methods are being developed for evaluating human health risk at petroleum contaminated sites.

3. OVERVIEW OF TPH

This section presents a historical perspective on the use of TPH in evaluating petroleum contaminated sites. Technical terms used in this section are explained in greater detail in subsequent sections. The use of TPH concentrations to establish target cleanup levels for soil or water is a common approach implemented by regulatory agencies in the United States. Approximately 75% of the states use TPH-based cleanup criteria. Because these values have become such key remediation criteria, it is essential that everyone using TPH data - environmental coordinators, field personnel, and regulators - be knowledgeable about the various analytical methods. It is important to know that minor method deviations may be found from state to state.

TPH is sometimes referred to as mineral oil, hydrocarbon oil, extractable hydrocarbon, and oil and grease. There are many analytical techniques available that measure TPH concentrations in the environment. No single method measures the entire range of petroleum-derived hydrocarbons .Because the techniques vary in the way hydrocarbons are extracted, cleaned up, and detected, they each measure slightly different subsets of the petroleum-derived hydrocarbons present in a sample. See Section 4. The definition of TPH depends on the analytical method used because the TPH measurement is the total concentration of the hydrocarbons extracted and measured by a particular method. The same sample analyzed by different TPH methods may produce different TPH values. For this reason, it is important to know exactly how each determination is made. Interpretation of the results depends on understanding the capabilities and limitations of the selected method. If used indiscriminately, TPH data can be misleading and could lead to an inaccurate assessment of risk.

There are several reasons why TPH data do not provide ideal information for investigating sites and establishing target cleanup criteria. For example, use of the term TPH suggests that the analytical method measures the combined concentration of all petroleum-derived hydrocarbons, thereby giving an accurate indication of site contamination. But this is not always the case. Furthermore, target cleanup levels based on TPH concentrations implicitly assume (1) the TPH result is an accurate measurement of petroleum-derived hydrocarbon concentration, and (2) the TPH result indicates the level of risk associated with the contamination. These assumptions are not correct due to many factors including the nonspecificity of some of the methods used and, the complex nature of petroleum hydrocarbons and their interaction with the environment over time.

One significant difficulty in measuring TPH for different product types is the fact that the boiling ranges and carbon number ranges of refined petroleum products often overlap. Refined petroleum products are primarily manufactured through distillation processes that separate fractions from crude oil by their boiling ranges. See Appendix III — Refinery Flow Diagrams. Manufacturing processes may also increase the yield of low molecular weight fractions, reduce the concentration of undesirable sulfur and nitrogen components, and incorporate performance enhancing additives. Additionally, because it is impossible to identify all constituents of a petroleum product, these constituents are often described by their boiling point ranges. Because distillations are not capable of producing sharp distinctions in boiling point cutoffs, there is overlap between distillate fractions. The boiling point ranges correlate to carbon number and the higher the carbon number, the higher the boiling point. However, structure will also influence boiling point. Branched and aromatic compounds of the same carbon number differ in boiling point from their corresponding n-alkane analogs. For these reasons, boiling point actually defines an approximate carbon range.

Figure 1 shows the relationship between boiling range and carbon number for some common petroleum products. This figure clearly shows the overlap between carbon ranges of different products as well as the overlap in corresponding analytical methods. For example, Figure 1 shows that an analytical method designed for gasoline range organics may report some of the hydrocarbons present in diesel fuel. The same is also true for analytical tests for diesel range organics that will identify some of the hydrocarbons present in gasoline contaminated soils. A more detailed discussion of boiling point and carbon number classification as well as a discussion of petroleum product composition, specification, product additives, and weathering is provided in Appendix II: Characterization of Petroleum Products.

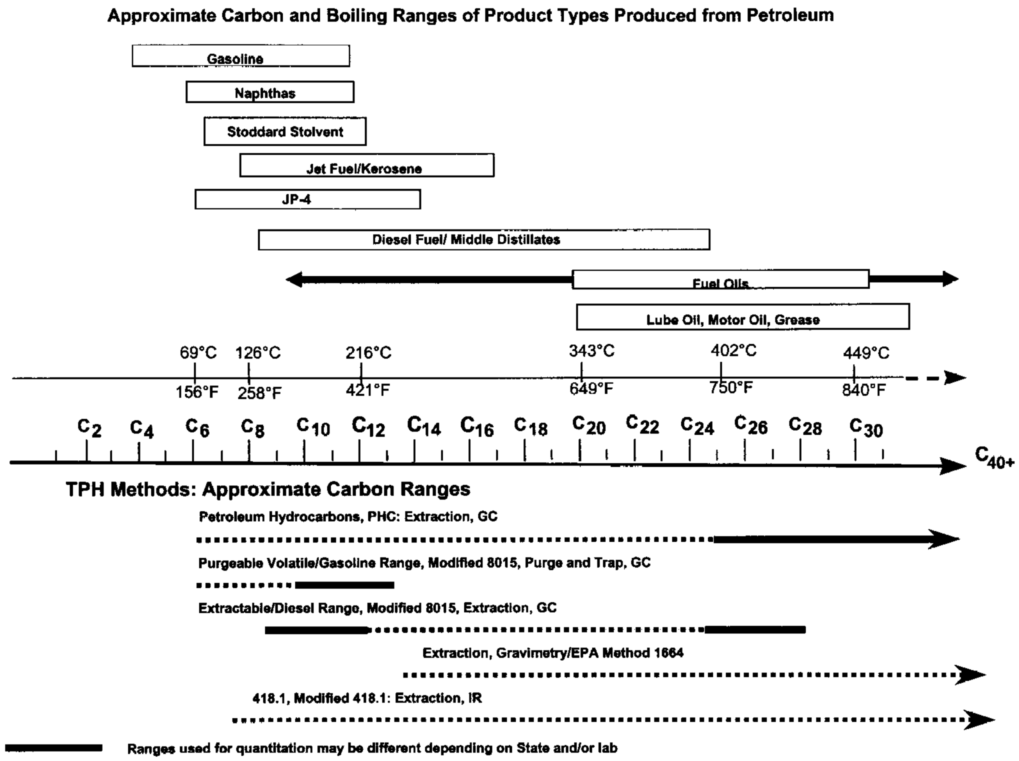


Figure 1. Summary of Petroleum Product Types and TPH and TPH Analytical Methods with Respect to Approximate Carbon Number and Boiling Point Ranges.

Ambiguous terminology associated with TPH methods presents additional difficulty in interpreting results. Each method has its own designation. For example, TRPH stands for total recoverable petroleum hydrocarbons, DRO stands for diesel range organics, GRO stands for gasoline range organics, and TPH-G stands for total petroleum hydrocarbons-gasoline. Frequently a method name that cites a product - "gasoline" or "diesel" - only implies a carbon range. For example, TPH-G does not necessarily imply that gasoline is present. These abbreviations may imply different carbon ranges to different laboratories or states. TPH methods are not optimized to identify product type. Even with improved, more detailed analytical methods, identification of aged products may prove difficult.

There is a reason for the availability of a large number of TPH measurement techniques. Because petroleum and petroleum-derived products are such complex mixtures, there is no single "best" method for measuring all types of petroleum contamination. As shown in Figure 1, some methods are appropriate for gasoline-contaminated samples while others are designed for heavier hydrocarbon contamination such as jet or diesel fuel. Some methods measure more compounds than other methods because they employ more rigorous extraction techniques or more efficient solvents. Other methods are subject to interferences from naturally occurring materials such as animal and vegetable oils, peat moss, dried grass, or humic material in topsoil, which may result in artificially high reported TPH concentrations. Some methods use cleanup steps to minimize the effect of nonpetroleum hydrocarbons, with variable success. Ultimately, methods are limited by the extraction and cleanup efficiency and measurement device detection limits.

The choice of a specific method should be based on compatibility with the particular type of hydrocarbon contamination to be measured. The choice may depend upon state regulatory requirements for the type of hydrocarbon contamination suspected to be present.

3.1 RISK IMPLICATIONS

TPH concentration data cannot be used to quantitatively estimate human health risk. The same concentration of TPH may represent very different compositions and very different risks to human health and the environment. For example, two sites may have TPH measurements of 500 ppm but constituents at one site may include carcinogenic compounds while these compounds may be absent at the other site. The risk at a specific site will change with time as contaminants evaporate, dissolve, biodegrade, and become sequestered. A valid correlation between TPH and risk would have to be site- and time-specific, related to a single spill, and, even then, the correlation might not be the same around the periphery of a plume where the rate of compositional change accelerates.

Although the utility of TPH data for risk assessment is minimal, it is an inexpensive tool that can be used for three purposes: (1) determining if there is a problem; (2) assessing the severity of contamination; and (3) following the progress of a remediation effort. If TPH data indicate that there may be significant contamination of environmental media, other data can be collected so that harm to human health can be quantitatively assessed. These other data can include target analyte concentration data and petroleum fraction concentration data obtained using new fraction-based analytical methods developed by the Working Group and others.

4. UNDERSTANDING THE PETROLEUM ANALYTICAL PROCESS: FROM SAMPLE COLLECTION TO MEASUREMENT

This volume focuses on three types of petroleum analytical methods:

- methods that measure a TPH concentration;
- methods that measure a petroleum group type concentration; and
- methods that measure individual petroleum constituent concentrations.

These three types of methods measure different petroleum hydrocarbons that might be present in petroleum-contaminated environmental media. TPH methods generate a single number that represents the combined concentration of all petroleum hydrocarbons in a sample, which are measurable by the particular method (See discussion in Section 3 regarding limitations of TPH data). Petroleum group type methods separate and quantify different categories of hydrocarbons (e.g., saturates, aromatics, and polars/resins). The results of petroleum group type analyses can be useful for product identification because different products (e.g., gasoline, fuel oil no.2, and jet fuel) can have characteristic levels of various petroleum groups (see Appendix II for a detailed characterization of petroleum products). Individual constituent methods quantify concentrations of specific compounds that might be present in petroleum-contaminated samples, such as benzene, ethylbenzene, toluene, and xylenes (BTEX), and polycyclic aromatic hydrocarbons (PAHs). Concentration data for individual petroleum constituents can be used to evaluate human health risk, provided the necessary toxicity data are available.

Although these three method types measure different petroleum hydrocarbon categories, there are several basic steps that are common to the analytical processes for all methods, no matter the method type or the environmental matrix. This section will focus on these basic steps. Sections 5, 6 and 7 review analytical methods that can provide the three different types of petroleum concentration data.

Most of the common analytical steps are related to the separation of analytes of interest from a sample matrix prior to their measurement. In general, these steps are:

- Collection and preservation - requirements specific to environmental matrix and analytes of interest
- Extraction - separates the analytes of interest from the sample matrix
- Concentration - enhances the ability to detect analytes of interest
- Cleanup - may be necessary to remove interfering compounds
- Measurement - quantifies the analytes.

Each step affects the final result, and a basic understanding of the steps is vital to data interpretation.

4.1 COLLECTION AND PRESERVATION OF ENVIRONMENTAL SAMPLES

The ability to collect and preserve a sample that is representative of the site is a critically important step. Obtaining representative environmental samples is always a challenge due to the heterogeneity of different sample matrices. Additional difficulties are encountered with petroleum hydrocarbons due to the wide range in volatility, solubility, biodegradation, and adsorption potential of individual constituents.

Most site investigations for assessment of petroleum hydrocarbon contamination in the environment are regulated by the states. However, sample collection and preservation recommendations follow U.S. EPA guidelines. A summary of the most commonly used guidelines is included in Table 1. It should be noted that there might be additional requirements in any given state. Before a sample is collected, the particular state requirements must be investigated. Because of holding time considerations, the laboratory must be selected and notified prior to the collection of the samples.

4.2 SAMPLE EXTRACTION

For most analyses, it is necessary to separate the analytes of interest from the matrix (i.e. soil, sediment, and water). Extraction of analytes can be performed using one or more of the following methods:

- Extracting the analytes into a solvent
- Heating the sample (used in the analyses of volatile compounds)
- Purging the sample with an inert gas (used in the analyses of volatile compounds).

There are a variety of common sample extraction techniques. See Table 2. Soxhlet, sonication, supercritical fluid, subcritical or accelerated solvent, and purge and trap extraction have been promulgated by the U.S. EPA as soil extraction methods. Headspace is recommended as a screening method. Shaking/vortexing is presently not approved by EPA, but is quite adequate for the extraction of petroleum hydrocarbons in most environmental samples.

For these extraction methods, the ability to extract petroleum hydrocarbons from soil and water samples depends on the solvent and the sample matrix. Surrogates (compounds of known identity and quantity) are frequently added to monitor extraction efficiency. Environmental laboratories also generally perform matrix spikes (addition of target analytes) to determine if analytes are retained by the soil or water matrix.

Solvents have different extraction efficiencies. Extracting the same sample in the same manner by two different solvents may result in different concentrations. The choice of solvents is determined by many factors such as cost, spectral qualities, method regulations, extraction efficiency, toxicity, and availability. Methylene chloride has been the solvent of choice for many semivolatile analyses due to its high extraction efficiency, low cost, and specification by many state regulatory methods. Chlorofluorocarbon solvents such as trichlorotrifluoroethane (Freon 113) have been used in the past for oil and grease analyses because of their spectral qualities (they do not absorb in the 2930 cm-1 infrared measurement wavelength) and low

TABLE 1. U.S. EPA-Recommended Sampling Protocols

			Sample Container[a]			
Analytical Parameter	**Analytical Method(s)**	**Media**	**Volume**	**Type**	**Preservatives[c]**	**Holding Time**
Trph[b]	EPA 418.1 (IR); Gravimetric;	water	1 liter	Glass jar with Teflon lined cap	acid fix pH < 2; cool to 4°C	extract in 7 days; analyze in 40 days
	GC/FID	soil	125 mL	Wide mouth glass Teflon lined cap	cool to 4°C	extract in 7 days; analyze in 40 days
Volatile Petroleum Hydrocarbons (VPH)[d]	various	water	40 mL	Glass vial with Teflon lined septum	acid fix pH < 2; cool to 4°C	14 days
		soil	40 mL	Glass vial with Teflon lined septum	cool to 4°C[e]	14 days
Extractable Petroleum Hydrocarbons (EPH)[f]	various	water	1 liter	Glass jar with Teflon lined cap	acid fix pH < 2; cool to 4°C	extract in 7 days; analyze in 40 days
		soil	60 mL	Wide mouth glass Teflon lined cap	cool to 4°C	extract in 7 days; analyze in 40 days
BTEX	EPA 8240/8260[h] EPA 8020/8021[h]	water	40 mL	Glass vial with Teflon lined septum	acid fix pH < 2; cool to 4°C	14 days
	EPA 624[g], EPA 602[g] EPA 524[g]	soil	40 mL	Glass vial with Teflon lined septum	cool to 4°C[e]	14 days
PAHs	EPA 8270[h] EPA 8310[h]	water	1 liter	Glass jar with Teflon lined cap	acid fix pH < 2; cool to 4°C	extract in 7 days; analyze in 40 days
	EPA 8100[h]	soil	60 mL	Wide mouth glass Teflon lined cap	cool to 4°C	extract in 7 days; analyze in 40 days

TABLE 1. (Continued)

[a] Minimum sampling volume may vary depending on specific method.

[b] Refers to extractable hydrocarbons only.

[c] ACID FIXATION: use 1:1 HCL to adjust pH of aqueous samples to less than 2. Add approx. 500µl (2-4 drops) to 40 mL aqueous sample vials; 5 mL to 1 liter aqueous sample jars. Add acid to vials before collecting sample; use gloves and eye protection when sampling. Other preservatives, such as sulfuric acid or sodium bisulfate may also be used for this purpose.

[d] Generally C_5 through $C_{10\pm2}$ hydrocarbons detectable through purge and trap or headspace analyses; includes most “Gasoline Range Organics” (GRO) methodologies.

[e] Some states/methodologies require field preservation of soil samples in methanol. In such cases, methanol must be purge and trap grade; typically, add 20 mL methanol to vials prior to sample collection. Use gloves and eye protection when sampling. Shipping of methanol subject to DOT regulation.

[f] Generally C_9 through $C_{28\pm7}$ hydrocarbons detectable through a solvent extraction process; includes most “Diesel Range Organics” (DRO) methodologies.

[g] 40 CFR Part 136.

[h] SW-846 methodology.

TABLE 2. Comparison of Common Extraction Techniques

Extraction Method	US SW-846 Method Number	Extraction Matrix	Compounds Extracted	Purpose
Separatory funnel	3510	water	semivolatile nonvolatile	laboratory
Continuous liquid-liquid	3520	water	semivolatile nonvolatile	laboratory
Solid phase extraction	3535	water	semivolatile nonvolatile	laboratory/ screening
Purge and trap	5030, 5035	water, soil	volatile	laboratory/ field preservation
Headspace	3810, 5021	water, soil	volatile	screening/ laboratory
Shake and vortex	[a]	soil	volatile semivolatile nonvolatile	screening/ laboratory
Soxhlet	3540, 3541	soil	semivolatile nonvolatile	laboratory
Sonication	3550	soil	semivolatile nonvolatile	laboratory
Supercritical fluid	3560, 3561	soil	semivolatile nonvolatile	laboratory
Subcritical fluid	3545	soil	semivolatile nonvolatile	laboratory

[a] Not an EPA SW-846 approved method.

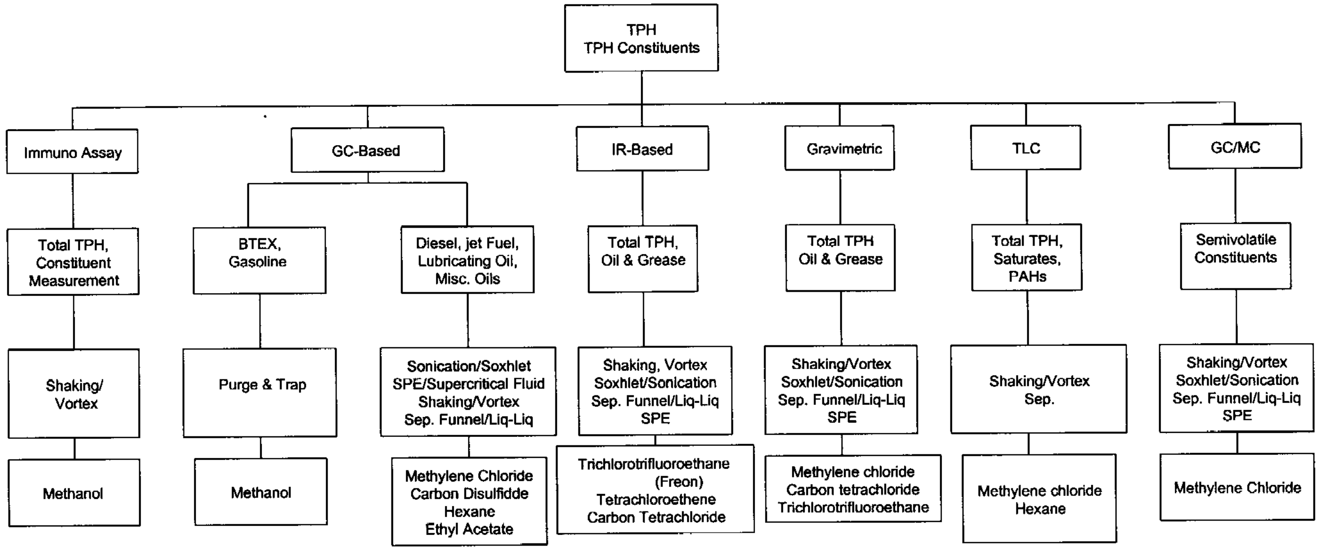


Figure 2. Solvent Choices for TPH and TPH Constituent Measurements.

human toxicity. The EPA is phasing out use of chlorofluorocarbons, however, due to their detrimental effects on stratospheric ozone. Tetrachloroethene and carbon tetrachloride are possible replacements. Methanol is the most common solvent used to preserve and extract volatiles such as BTEX in soils. Figure 2 illustrates the typical solvents used for different analyses.

Water Samples

Water extraction methods in common use include the following:

For Volatiles:

- Purge and trap
- Headspace

For Semivolatiles:

- Separatory funnel extraction
- Continuous liquid-liquid extraction
- Solid phase extraction.

Volatile compounds (gasoline, solvents) in water are generally separated from their matrix by purging with an inert gas and trapping the compounds on a sorbent (EPA 5030, purge and trap analysis). The sorbent is later heated to release the volatile compounds, and a carrier gas sweeps the compounds into a gas chromatograph.

Headspace analysis is recommended as a screening method by EPA (Methods 3810, and 5021), although it performs well in particular situations, especially field analysis. In this method, the water sample is placed in a closed vessel with a headspace and heated to drive volatiles into the gas phase. Addition of salts or acids may enhance this process. In headspace analysis, instrument contamination is minimized because only volatile compounds are introduced into the instrument. Samples containing heavy oils and high analyte concentrations can severely contaminate purge and trap instrumentation.

The most commonly used water extraction method for semivolatiles is EPA Method 3510, separatory funnel extraction. The sample is poured into a funnel-shaped piece of glassware, solvent is added, and the mixture is shaken vigorously. After layer separation, the extract (i.e., the solvent layer) is removed, filtered, dried with a desiccant, and concentrated. Multiple extractions on the same sample may increase overall recovery.

Another commonly used water extraction method for semivolatiles is EPA 3520, continuous liquid-liquid extraction. Rather than shaking solvent with the water sample, the solvent is continuously heated, nebulized (broken into small droplets), and sprayed on top of the water. Liquid-liquid extraction is excellent for samples containing emulsion-forming solids, but it is more time-consuming than separatory funnel extractions.

Solid phase extraction (SPE, EPA Method 3535) also can be used for extraction and concentration of semivolatile material. The technique involves passing the water sample through a cartridge or disk containing an adsorbent such as silica or alumina. The adsorbent is often coated with compounds that impart selectivity for particular products or analytes such as PAHs. After extraction, the analytes are separated from the solid phase by elution with a small amount of organic solvent. A variant of SPE involves dipping a sorbent-coated fiber into the water (solid phase micro-extraction, or SPME). Adsorbed analytes are thermally desorbed directly into a heated chromatographic injection port. SPE uses much less solvent and glassware than separatory funnel and liquid-liquid extraction.

Soil Samples

Soil extraction methods in common use include the following:

For Volatiles:

- Purge and trap
- Headspace

For Semivolatiles:

- Shaking or vortexing (can also be used for volatiles)
- Soxhlet
- Sonication
- Supercritical fluid
- Subcritical fluid.

Volatile compounds (e.g., BTEX and gasoline) may be solvent-extracted from soil. EPA Method 5035, purge and trap analysis, specifies a methanol extraction, which is usually done by mechanical shaking of the soil with methanol. A portion of the methanol extract is added to a purge vessel and diluted in reagent grade water. The extract is then purged similar to a water sample.

Headspace analysis, (EPA Methods 3810 and 5021), also works well for analyzing volatiles in soils. The soil is placed in a headspace vial and heated. Salts can be added to more efficiently drive out the volatiles from the sample into the headspace of the sample container. Similar to water headspace analysis, the soil headspace technique is useful when heavy oils and high analyte concentrations are present which can severely contaminate purge and trap instrumentation. Detection limits are generally higher for headspace analysis than for purge and trap analysis.

The simplest method to separate semivolatile compounds from soils is to shake or vortex (vigorous mechanical stirring) soil with a solvent. Adding a desiccant to the soil/solvent mixture can help to break up soil and increase the surface area. The extract can be analyzed directly. Simple shaking is quick and easy, making it an excellent field extraction technique. However, extraction efficiency may vary depending on soil type.

Soxhlet extraction (EPA Method SW-846 3540) is a very efficient extraction process which is commonly used for semivolatiles. Solvent is heated and refluxed (recirculated) through the soil sample continuously for 16-24 hours or overnight. This method generates a relatively large volume of extract that needs to be concentrated. Thus, it is more appropriate for semivolatiles than for volatiles.

Sonication extraction (EPA Method SW-846 3550) can also be used for semivolatiles, it involves the use of sound waves to enhance analyte transfer from sample to solvent. Sonication is a faster technique than Soxhlet extraction, and it also can require less solvent.

Supercritical fluid extraction (SFE), (EPA Methods 3540 for Total Recoverable Petroleum Hydrocarbons and 3561 for PAHs), is applicable to the extraction of semivolatiles. SFE involves heating and pressuring a mobile phase to supercritical parameters (having properties of gas and liquid). The supercritical fluid is passed through the soil sample, and the analytes are concentrated on a sorbent or trapped cryogenically. The analytes are eluted with a solvent and analyzed with conventional techniques. CO_2 is the most popular mobile phase.

Proposed EPA Method 3545, Accelerated Solvent Extraction, has extraction efficiencies comparable to Soxhlet extractions. This method is sometimes referred to as subcritical fluid extraction. Conventional solvents such as methylene chloride are heated and pressurized, then passed through the soil sample (this technique also works for sludges and sediments). Subcritical fluid extraction has the advantage of requiring smaller solvent volumes than traditional solvent extraction techniques.

Free Phase Hydrocarbon Samples

In some releases of petroleum products to the environment where free phase product is found, hydrocarbon material can be collected directly for characterization. The ability to analyze free product greatly aids the determination of product type and potential source. The samples may be diluted prior to analysis. EPA Method SW-846 3580, waste dilution, gives some guidelines for proper dilution techniques.

4.3 CONCENTRATION OF SAMPLE EXTRACT

Extracts are generally filtered, dried with desiccant, and concentrated before analysis. Concentration of the extract may allow for lower sample detection limits. Frequently, sample extracts must be concentrated to obtain detection limits low enough to meet regulatory action limits. Concentration may be achieved by:

For Volatiles:

- Sorbent trapping
- Cryogenic trapping

For Semivolatiles:

- Snyder column
- Kuderna Danish concentrator
- Nitrogen evaporation
- Vacuum.

The trapping step in a purge and trap analysis is essentially a concentration step. Analytes are purged from the matrix into a gas stream and captured on a sorbent trap. The analytes are released by heating the trap. Some laboratories use cryogenic trapping in place of sorbent trapping. A very cold material such as liquid nitrogen surrounds a sample loop. As analytes are purged and swept through the sample loop, they freeze in the sample loop. The analytes are released when the trap is heated.

Snyder columns are designed to allow highly volatile solvents to escape while retaining semivolatile analytes of interest. Snyder columns are generally fitted onto the tops of flasks containing extracts. The column design permits solvent to escape as the flask is heated. The analytes of interest condense from a gas to a liquid phase and fall back down into the solvent reservoir. The Kuderna-Danish concentrator is a Snyder column with a removable collection tube attached to the bottom. As solvent is evaporated, the extract is collected in the collection tube.

As an alternative to a Snyder column, the sample extracts may be concentrated with nitrogen evaporation by directing a slow stream of the gas over the extract surface at room temperature, resulting in minor loss of volatiles. Placing the extract container in warm water helps to speed the process, but then some loss of volatiles can occur.

Concentration by evaporating excess solvent with a vacuum is not very common in environmental laboratories. Many semivolatile analytes are lost in the procedure. Additionally, evaporating as a means of concentrating the sample cannot be used if the goal is to detect volatile analytes.

4.4 CLEANUP OF SAMPLE EXTRACT

Cleanup steps can be an important component of infrared (IR)-based and gravimetric methods because these methods are very sensitive to nonpetroleum hydrocarbon interferences. Cleanup steps are less commonly utilized for gas chromatography (GC)-based methods because experienced GC analysts can recognize the presence of interfering compounds (e.g., animal- and vegetable-derived hydrocarbons).

Cleanup steps are not always a part of the petroleum analytical process, but when they are necessary, the goals of extract cleanup steps typically include one or more of the following:

- Removal of nonpetroleum compounds
- Isolation of a particular petroleum fraction
- Concentration of analytes of interest.

The techniques employed to extract the analytes of interest can frequently extract interfering compounds. Polar compounds such as animal and plant fats, proteins, and small biological molecules may be improperly identified as petroleum constituents. Extract cleanup techniques can be used to remove them. In an ideal situation, only interfering compounds are removed. In reality, some polar petroleum constituents can also be removed.

Two techniques are used to clean petroleum extracts. In one technique, interfering compounds are removed by passing the extract through a glass column filled with sorbent. A second technique is to swirl the extract with loose sorbent, then remove the sorbent by filtration.

Three of the EPA-promulgated cleanup techniques involve trapping the interfering compounds on a sorbent column. EPA SW-846 3611 is an alumina cleanup designed to remove interfering compounds and to fractionate petroleum wastes into aliphatic, aromatic and polar fractions. The fractions can be analyzed separately or combined for a total TPH measurement. EPA SW-846 3630, silica gel cleanup, is the most common cleanup technique used on extracts designated for PAHs and phenol analyses. Variations of this technique are used to clean EPA Method 418.1 extracts before IR analysis. EPA Method SW-846 3640, gel-permeation cleanup, works on the principle of size exclusion. Large macromolecules such as lipids, polymers, and proteins are removed from the sample extract. Extracts obtained from soils with high biological activity may be cleaned by this method.

There are two noncolumn EPA-promulgated cleanup techniques. EPA SW-846 3650, acid-base partition can be used to separate the base/neutral and acid components by adjusting pH. Very often, only one fraction contains the compounds of interest. This technique is often used before alumina column cleanup to remove the acid components. EPA Method SW-846 3660 is used for sulfur removal. This technique uses copper, mercury, and tetrabutylammonium sulfite as desulfurization compounds. Sulfur is a common interfering compound for petroleum hydrocarbon analysis, particularly for sediments. Sulfur-containing compounds are very common in heavy fuels and crudes and on refinery sites. Elemental sulfur is often present in anaerobically biodegraded fuels. High levels of sulfur may be measured as “TPH” by some techniques if the cleanup technique is not used.

Solid phase cartridges for sample cleanup are available from chromatography suppliers. These cartridges are available in a wide variety of adsorbents with unique chemical selectivities; however, they have limited capacity.

There can be several limitations to various cleanup steps. Reasons for decreased effectiveness of cleanup procedures include:

- Sample loading may exceed the capacity of cleanup columns and cartridges.
- Nonpetroleum compounds may have chemical structures similar to petroleum compounds and may behave like a petroleum compound. These compounds evade cleanup.
- The cleanup may not have been done properly (poor technique).
- Some analytes of interest may be removed.
- There may be cases in which no single cleanup technique removes all interferences.

For example, Table 3 shows the results of serial silica gel cleanups of EPA Method 418.1 extracts of plant materials. These results illustrate the limited effectiveness of multiple silica gel cleanups for the removal of biogenic hydrocarbon interferences.

4.5 MEASUREMENT

Once the sample preparation is complete, there are several approaches for detecting and quantifying petroleum hydrocarbons:

- Total petroleum hydrocarbon (TPH) measurement
- Petroleum group type measurement
- Individual component measurement.

TABLE 3. Effect of Silica Gel on Removing Biogenic Hydrocarbon Interferences from Vegetative Materials (Freon-113 Extracts)[a]
TPH concentrations given in ppm (mg/kg)

Vegetable Material	Prior to Addition of Silica Gel	After First Addition of Silica Gel	After Second Addition of Silica Gel	After Third Addition of Silica Gel
Fresh pine needles	16,000	1,700	1,400	—
Pine bark	2,400	380	370	—
Pine needle compost	1,200	70	67	—
Maple tree seeds	7,100	1,600	1,500	—
Oak leaves dried	18,000	4,800	4,600	—
Grass, dried	14,000	4,500	2,700	2,600
Gall nuts	9,700	4,500	1,300	1,200

[a] Source: Data from “EPA Method 418-1 Total Recoverable Petroleum Hydrocarbons by IR”, *Groundwater Analytical Bulletin*, (Buzzards Bay: Groundwater Analytical Inc. 1991).

Total Petroleum Hydrocarbon (TPH) Measurement

Total petroleum hydrocarbon (TPH) measurements are conducted to determine the total amount of hydrocarbon present in the environment. There are a wide variety of TPH methods. In practice, TPH is defined by the method used to analyze it. Different methods often give different results because they are designed to extract and measure slightly different subsets of petroleum hydrocarbons. No single method gives a precise and accurate measurement of TPH for all types of contamination. The four most commonly used TPH testing methods include gas chromatography (GC), infrared spectrometry (IR), gravimetric analysis, and immunoassay.

Petroleum Group Type Measurement

Petroleum group type measurements are conducted to determine amounts of various petroleum compound classes (e.g., saturates, aromatics, and polars/resins) present in a petroleum contaminated samples. Compound classes are discussed in detail in Appendix I. This type of measurement is sometimes used to identify fuel type or to track plumes. It may be particularly useful for heavier hydrocarbons such as tar and asphalt. Group type test methods include multidimensional gas chromatography (not often used for environmental samples), high performance liquid chromatography (HPLC), and thin layer chromatography (TLC).

Petroleum Constituent Measurement

Methods that analyze individual compounds (e.g., BTEX and PAHs) are generally run to detect the presence of an additive or to provide concentration data needed to estimate human health risk associated with individual compounds. Common constituent measurement techniques include gas chromatography with second column confirmation, gas chromatography with multiple selective detectors and gas chromatography with mass spectrometry detection (GC/MS).

5. TOTAL PETROLEUM HYDROCARBON (TPH) MEASUREMENT: DETAILED REVIEW OF SELECTED ANALYTICAL METHODS

A TPH method generates a single number quantifying the amount of petroleum that is measured by the specified technique. The most popular TPH methods are based on gas chromatographic (GC), infrared (IR), or gravimetric analytical techniques. GC-based methods are currently the preferred laboratory methods for TPH measurement because they detect a broad range of hydrocarbons, they provide both sensitivity and selectivity, and they can be used for TPH identification as well as quantification. IR-based methods have been widely used in the past for TPH measurement because they are simple, quick and inexpensive. However, their use is currently decreasing due to the worldwide ban on Freon production (needed for sample extraction and measurement), the nonspecificity of these methods, and their inability to provide any information on TPH identification and potential risk. Gravimetric-based methods are also simple, quick, and inexpensive, but they suffer from the same limitations as IR-based methods. Gravimetric-based methods may be useful for very oily sludges and wastewaters, which will present analytical difficulties for other more sensitive methods. Immunoassay TPH methods are gaining popularity for field testing because they offer a simple, quick technique for in-situ TPH quantification.

The following four sections provide detailed descriptions of these TPH methods. Each section provides an overview of the analytical technique, example methods, the purpose of the method (i.e., what it is intended to measure), and key interferences/limitations. Table 4 briefly summarizes this information for each TPH analytical method for quick reference. Appendix IV includes tables that provide more detailed information about published GC-based and non-GC TPH methods. These tables provide method-specific information for EPA and state methods, including recommendations for method use, common interferences, procedural notes, advantages, and disadvantages.

5.1 GAS CHROMATOGRAPHY (GC) TPH METHODS

For GC-based methods, TPH is defined as anything extractable by a solvent or purge gas and detectable by gas chromatography/flame ionization detection (GC/FID) within a specified carbon range. The primary advantage of GC-based methods is that they provide information about the type of petroleum in the sample in addition to measuring the amount. Identification of product type(s) is not always straightforward, however, and requires an experienced analyst of petroleum products. Detection limits are method- and matrix-dependent and can be as low as 0.5 mg/L in water or 10 mg/kg in soil.

Overview of the Technique

Gas chromatography is a technique that separates mixtures. “A mixture of chemicals is separated into its individual components as the sample travels through a column in the gas chromatograph. Separation is achieved by a combination of factors including boiling point, polarity, and affinity differences among the different components in the sample. The time a compound spends on a specific column is called the retention time and it is reproducible. The retention time is characteristic of a compound under given experimental parameters and specified column. As the separated components elute from the column, they are detected” (Swallow et al., 1988). The detector signal is proportional to the amount of compound present.

Chromatographic columns are commonly used to determine TPH compounds approximately in the order of their boiling points. Compounds are detected with a flame ionization detector, which responds to virtually all compounds that can burn. The sum of all responses within a specified range is equated to a hydrocarbon concentration by reference to standards of known concentration.

Two techniques are most commonly used to get the samples into the column.

- Purge and trap systems purge components out of water or water/methanol by bubbling gas through the liquid. The components are concentrated on a very short intermediate column or “trap,” which is heated to drive them onto the

TABLE 4. General Summary of Analytical Methods for TPH Measurement

Method Name	Method Type/ Environmental Media	Typical Products Detected	Typical Carbon Ranges Detected	Published Methods
GC-Based TPH methods	primarily laboratory but also field applications- can be adapted for all media	primarily gasolines, diesel fuel, and fuel oil #2 - can be modified for heavier hydrocarbon mixtures (e.g., lubricating oils, heavy fuel oils)	normally between C6 and C25 or C36 (can be modified for higher carbon numbers)	EPA Method 8015B, state-modified 8015 methods
IR-Based TPH methods	laboratory and field screening - most appropriate for water and soil	primarily diesel and fuel oils	most hydrocarbons with exception of volatile and very high hydrocarbons	EPA Method 418.1
Gravimetric TPH methods	laboratory - most appropriate for wastewaters, sludges, and sediment	most appropriate for heavier petroleum products (e.g., crude oils, lubricating oils, etc.)	anything that is extractable (with exception of volatiles which are lost)	EPA Method 9071; EPA proposed Method 1664
Immunoassay TPH methods	field screening - most appropriate for soil and water	various products (but yields only screening numbers)	aromatic hydrocarbons (e.g., BTEX, PAHs)	EPA Method 4030

TABLE 4.

Detector Type	Approximate Detection Limits	Key Advantages	Interferences/ Limitations
GC/FID	can be as low as 0.5 mg/L in water, 10 mg/kg in soil	can detect broad range of hydrocarbon compounds; simple and sensitive; can provide information (e.g., a chromatogram) for product identification	normally cannot detect compounds below C6; may not detect polar hydrocarbons (e.g., alcohols, ethers, etc.); chlorinated solvents may be quantified as TPH
IR spectrometer	1 mg/L in water; 10 mg/kg in soil	technique is simple, quick, and inexpensive	Freon is now banned; lack of specificity; low sensitivity; high loss of volatiles; poor extraction of high molecular weight hydrocarbons; prone to interferences; provides quantitation only
Gravimetric balance	5 to 10 mg/L in water; 50 mg/kg in soil	technique is simple, quick, and inexpensive	Freon is banned, although other solvents are available; lack of specificity; low sensitivity; high loss of volatiles; prone to interferences; provides quantitation only
Portable test kit	200 to 500 ug/L in water; 10 to 500 mg/kg in soil	technique is simple, quick, inexpensive, and can be done in the field	low sensitivity; can detect interferences; primarily only measure aromatics; low accuracy and precision; should only be used as screening measurement; provides quantitation only

analytical column where they are separated. Hydrocarbons from C_5 through about C_{12} can be analyzed using this technique. Purge and trap sample introduction is used for light products such as gasoline and condensate.

- Direct injection involves taking the hydrocarbon, diluted hydrocarbon, or an extract of hydrocarbon into a syringe and injecting it into the gas chromatograph. This technique can be used for any type of hydrocarbon, but it is most frequently used for distillates, lube oils and crude oils.

Headspace sample introduction can be used for the determination of light hydrocarbons, and it is most often used for field screening.

Example Methods

Prior to 1997, EPA SW-846 Methods 8015 and 8015A were often quoted as the source of GC-based TPH methods, commonly referred to as "Modified 8015." However, the original 8015 methods were titled "Nonhalogenated Volatile Organics" and were designed to measure a short target list of chemical solvents rather than petroleum hydrocarbons. Because there was no universal method for petroleum hydrocarbons, each state specified its own version. The recent Update III of EPA SW-846, 3rd Ed. includes a new Method 8015B titled "Nonhalogenated Volatile Organics Using GC/FID", with guidance for the analysis of gasoline and diesel range organics. Whether the new method will replace the many techniques currently in use is uncertain. The current individual methods differ in procedure, compounds detected, extraction techniques and extraction solvents used. Some methods may include a cleanup step to remove biogenic (bacterial or vegetation-derived) material while others do not. The methods have in common a boiling point-type column and a flame ionization detector.

Some regulatory agencies specify two GC-based TPH methods. Selection of a method depends on the type of hydrocarbon suspected to be in the sample:

- If gasoline is suspected to be the sole contaminant, the TPH method will use purge/trap sample introduction. Many of these methods are referred to as volatile range organics - TPHV, TPH-G, or GRO - gasoline range organics. Typically, gasoline or a synthetic mixture will be used to prepare calibration standards.

- If heavier petroleum fractions (diesel, middle distillates, motor oil) are the contaminants, the analysis will use direct injection and hotter oven temperatures. Many of these methods are referred to as extractable range organics, TPH-D or DRO - diesel range organics. Typically, diesel fuel #2 or a synthetic mixture will be used to prepare calibration standards. Jet fuel or lube oil may be used when appropriate.

- Mixtures or unknown contamination may require both volatile range and extractable range analyses. Alternately, a single injection can be used to analyze the whole sample, but the extraction method must not use a solvent evaporation step. Reporting limits for a single injection method are approximately 20 mg/L.

What Do GC Methods Measure?

A GC/FID will detect any hydrocarbons that elute from the column and burn. The analog signal from the detector is called a chromatogram. GC/FID methods specify a certain portion of the chromatogram (a "window" or carbon number range) for quantification. The carbon number range will approximate that of the fuel of interest - gasoline, diesel, or heavier hydrocarbon. The carbon number range specified for each fuel may differ from state to state. Volatile compounds that elute before the solvent peak (usually those $< C_6$) are typically not measured.

GC-based methods can be broadly used for different kinds of petroleum releases but are most appropriate for detecting nonpolar hydrocarbons with carbon numbers between C_6 and C_{25} or C_{36}.

Many lube oils contain molecules with more than 40 carbon atoms. Crude oils may contain molecules with 100 carbons or more. These heavy hydrocarbons are outside the detection range of the more common GC-based TPH methods, but specialized gas chromatographs are capable of analyzing such heavy molecules. Accurate quantification depends on adjusting the chromatograph to reach as high a carbon number as possible, then running a calibration standard with the same carbon range as the sample. The lab must also check for mass discrimination, a tendency for heavy molecular weight hydrocarbons to be retained in the injection port. Labs should be notified if a sample is suspected to be heavy oil, or to contain a mixture of light and heavy oils, so that they can use the appropriate GC method. Gravimetric or IR methods are often preferred for very heavy samples. They can even be used as a check on GC/FID results if it is suspected that heavy molecular weight hydrocarbons are present but are not being detected. Laboratories should flag data if heavy material is observed in the chromatogram, even if this material cannot be quantified.

Calibration standards vary. Most methods specify a gasoline calibration standard for volatile range TPH and a diesel fuel #2 standard for extractable range TPH. Some methods use synthetic mixtures for calibration. Because most methods are written for gasoline or diesel fuel, TPH methods may have to be adjusted to measure contamination by heavier hydrocarbons - lubricating oils, heavy fuel oils, or crude. Such adjustments may entail use of a more aggressive solvent, a wider GC "window" - up to C_{36} or more - and a different calibration standard that more closely resembles the "heavier" contamination.

GC-based methods can be modified and fine-tuned so that they are suitable for measurement of specific petroleum products or group types. Examples of modified GC-based methods include GRO, DRO, and TPHV methods. These modified methods can be particularly useful when there is information on the source of contamination, but method results should be interpreted with the clear understanding that a modified method was used for detection of a specific carbon range. It is essential that the user understand what hydrocarbons a GC-based method can and cannot detect and how results are quantified. For example, BTEX is a subset of TPHV. If benzene, toluene, ethylbenzene, and the three xylene isomers are present in a sample, they will be quantified along with the other TPHV components. The TPHV measurement typically is greater than the sum of the BTEX measurements. Gasoline should not be quantified by adding the TPHV and BTEX quantities together.

Interpretation of GC-based TPH data can be complicated and the analytical method should always be considered when interpreting concentration data. A volatile range TPH analysis may be very useful for quantifying TPH at a gasoline release site, but a volatile range TPH analysis will not detect the presence of lube oil. In addition, a modified GC-based method which has been specifically selected for detection of gasoline-range organics at a gasoline-contaminated site may also detect hydrocarbons from other petroleum releases because fuel carbon ranges frequently overlap (See discussion in Section 3). Gasoline is found primarily in the volatile range. Diesel fuel falls primarily in an extractable range. Jet fuel overlaps both the volatile and semivolatile ranges. However, the detection of different kinds of petroleum does not necessarily indicate that there have been multiple releases at a site. Analyses of spilled waste oil will frequently detect the presence of gasoline, and sometimes diesel. This does not necessarily indicate multiple spills. All waste oils contain some fuel. As much as 10% of used motor oil can consist of gasoline (Owen and Coley, 1990). The fuel gets into the oil as combustion chamber gases blowing past the piston rings - a more pronounced problem in high mileage engines with worn rings. Liquid fuel will also seep past rings under cold start and warm-up conditions (Rhodes et al., 1994).

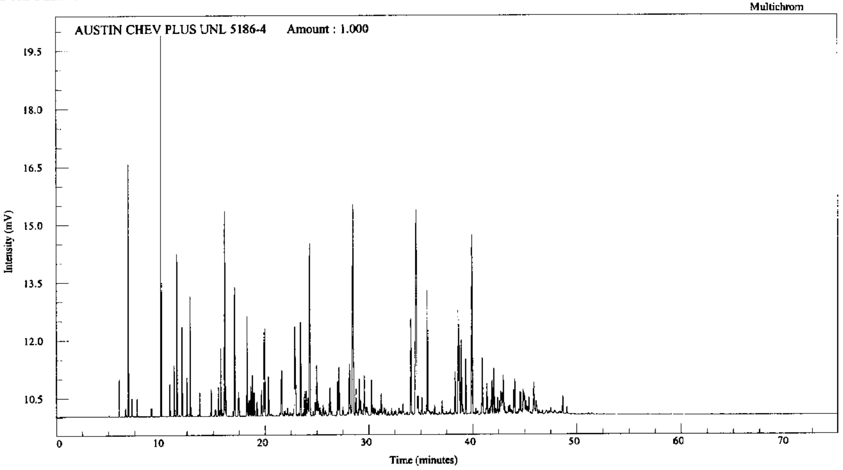
If the type of contaminant is unknown, a “fingerprint” analysis can help identify it. A “fingerprint”, or pattern recognition, analysis is a direct injection GC/FID analysis where the chromatogram is compared to chromatograms of reference materials. Certain fuels can be identified by characteristic, reproducible chromatographic patterns. For example, chromatograms of gasoline and diesel differ considerably, as shown in Figures 3 and 4. There are complicating factors, however. Many hydrocarbon streams may have similar fingerprints. Diesel #2 and #2 fuel oil both have the same boiling point range and chromatographic fingerprint. A fingerprint can be used to conclusively identify a mixture when a known sample of that mixture or samples of the mixture’s source materials are available as references. As a fuel evaporates or biodegrades, its pattern can change so radically that identification becomes difficult. Consequently, a GC “fingerprint” is not a conclusive diagnostic tool. These chromatograms must be interpreted by experienced analysts. While GC-based TPH and pattern recognition methods are very similar, TPH methods stress calibration and quality control, while pattern recognition methods stress detail and comparability.

Interferences/Limitations

The GC-based methods usually cannot quantitatively detect compounds below C_6 because these compounds are highly volatile and interference can occur from the solvent peak. As much as 25% of fresh gasoline can be below C_6. This is not a problem for the analyst with weathered gasoline range and/or diesel range contamination because most of the very volatile hydrocarbons ($<C_6$) may no longer be present in the sample.

GC-based TPH methods may also have problems quantifying polar hydrocarbon constituents (nitrogen, oxygen, and sulfur containing molecules). Some polar hydrocarbon constituents are too reactive to pass through a gas chromatograph and thus will not reach the detector for measurement.

Gasoline



Diesel #2

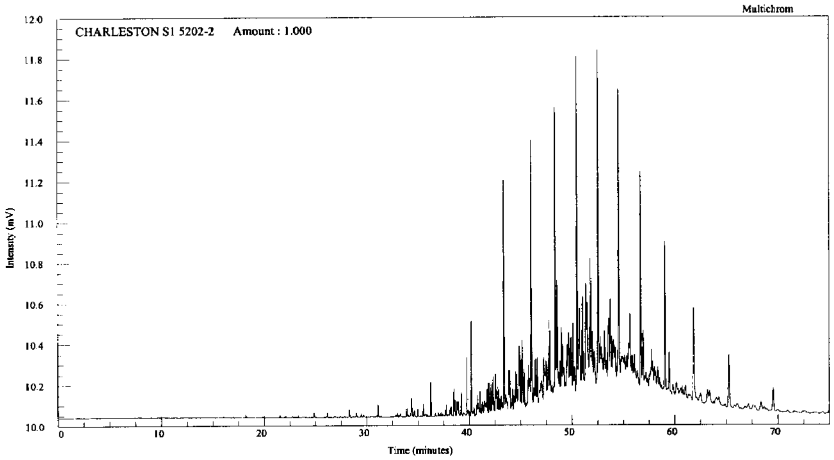
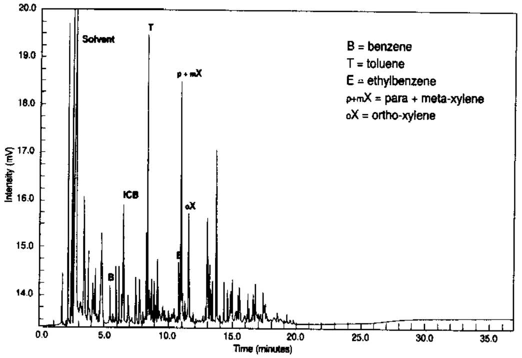
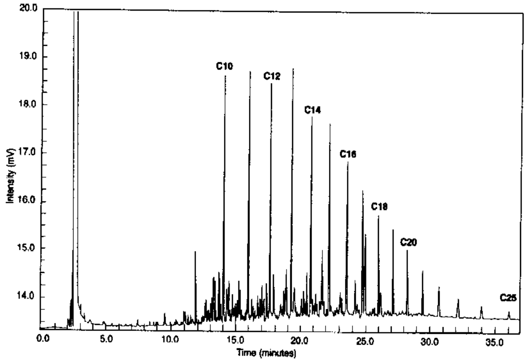


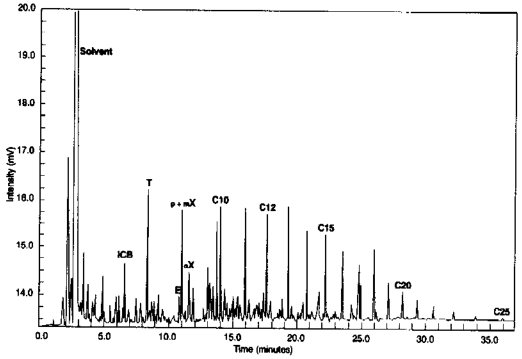
Figure 3. Gas Chromatograms of Fuels.



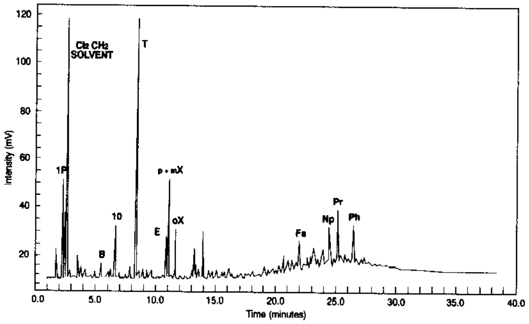
Chromatogram of Extract from Spiked Soil.
2300 PPM Gasoline in Soil.



Chromatogram of Extract from Spiked Soil.
2700 PPM Diesel in Soil.



Chromatogram of Extract from Spiked Soil.
2200 PPM Gasoline Plus Diesel (1:1).



Chromatogram of Extract from Soil Sample Containing Gasoline and Extremely Weathered Diesel Range Material.

Figure 4. GC "Fingerprint" Chromatograms of Soil Contamination.

Oxygenated gasolines are sometimes analyzed by GC-based methods. Efficiency of purge methods is lower for oxygenates such as ethers and alcohols. GC detector response to oxygenates is lower relative to hydrocarbons. Therefore TPH results will tend to be biased slightly low for ether-containing fuels compared to equivalent amounts of traditional gasolines. Methanol and ethanol elute before C_6; consequently, they are not quantified and may not even be detected due to coelution with the solvent. TPH results for fuels containing these alcohols also will have a negative bias.

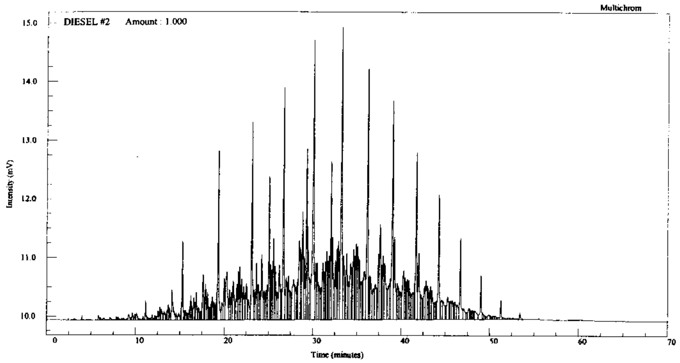
GC-based methods may overestimate TPH concentrations due to the detection of non-petroleum compounds. Chlorinated compounds may be detected by GC-based methods and reported as TPH. While leaded gasolines contain a few parts per million 1,2-dichloroethane and 1,2-dibromoethane as part of the lead additive package, unleaded gasolines contain no chlorinated compounds. Solvents such as tetrachloroethene and trichloroethane may come from dry cleaning operations, parts degreasing, and semiconductor manufacturing. In addition, cleanup steps do not perfectly separate petroleum hydrocarbons from biogenic material. Plant oils and waxes are sometimes extracted from vegetation-rich soils and quantified by GC methods as TPH. Silica gel cleanup may help to remove this interference but may also remove some polar hydrocarbons.

Because petroleum is made up of so many isomers, many compounds, especially those above about C_8, coelute with isomers of nearly the same boiling point. These unresolved compounds are referred to as the unresolved complex mixture (UCM). They are legitimately part of the petroleum signal, and unless state regulations specify otherwise, should be quantified. Quantifying UCM requires a baseline-to-baseline integration mode rather than a peak-to-peak integration mode, as shown in Figure 5. Baseline to baseline integration quantifies all hydrocarbons in a sample including the UCM, while in the peak-to-peak integration mode, only the individual resolved hydrocarbons (not including the UCM) are quantified. Laboratories rarely report integration modes; therefore, it is wise to ask what integration mode has been used. Some researchers argue that the UCM also may contain some bacterial metabolites of petroleum hydrocarbons, generally alcohols, aldehydes and acids. However, many of these polar compounds will not pass through a chromatographic column and others can be removed with silica gel.

5.2 INFRARED SPECTROSCOPY (IR) TPH METHODS

For IR-based methods, TPH is defined as anything extractable by a solvent (Freon 113), which is not removed by silica gel and can be detected by IR at a specified wavelength. The primary advantage of IR-based TPH methods is that they are simple, quick and inexpensive. Detection limits for a commonly used IR-based TPH method, EPA Method 418.1, are approximately 1 mg/L in water and 10 mg/kg in soil. This TPH method often suffers from poor accuracy and precision, especially for heterogeneous soil samples. IR-based methods give no information on the type of fuel present, no information about the presence or absence of toxic molecules, and no specific information about potential risk associated with the contamination.

Baseline to Baseline



Peak to Peak

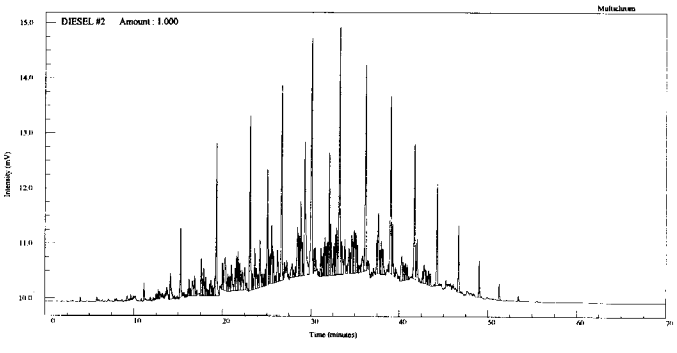


Figure 5. Integration Modes.

Overview of the Technique

Infrared spectroscopy measures the vibration (stretching and bending) that occurs when a molecule absorbs energy (heat) in the infrared region of the electromagnetic spectrum. Different functional groups and bond types have different IR absorption frequencies and intensities.

IR-based TPH methods measure the absorbance of the C-H bond. Most IR-based methods in the United States typically measure the absorbance at a single frequency (usually 2930 cm^{-1}) which corresponds to the stretching of aliphatic CH_2 groups. Some methods, especially in Europe, use multiple frequencies including 2960 cm^{-1} for CH_3 groups and 2900 to 3000 cm^{-1} for aromatic C-H bonds.

Samples are extracted with a suitable solvent (i.e., a solvent with no C-H bonds). Biogenic polar materials are removed with silica gel. Some polar petroleum hydrocarbons may be lost in the silica gel cleanup. The absorbance of the silica gel eluate is measured at the specified frequency and compared to the absorbance of a standard or standards of known petroleum hydrocarbon concentration. The IR absorbance is a measurement of the sum of all the compounds contributing to the TPH result. IR-based TPH methods cannot provide information on the type of hydrocarbon contamination.

The extraction solvent for measuring TPH in soil must not contribute any C-H stretching to the measurement. The most frequently specified solvent has been Freon-113. This solvent is no longer being manufactured, in accordance with the Montreal Protocol on Substances that Deplete the Ozone Layer and the Clean Air Act Amendments of 1990. Some labs are depleting stockpiled Freon or redistilling used Freon. Others have switched to alternate solvents. Carbon tetrachloride has been used for IR-based methods (mostly in the European community). It is in limited use in the U.S. because it is a known carcinogen and also affects the ozone layer. Tetrachloroethene (also known as perchloroethylene, or PERC) is currently being used by some U.S. labs. Solvents such as methanol, methylene chloride, or hexane are not suitable for an IR-based method because they contain C-H bonds.

For all IR-based TPH methods, the C-H absorbance is quantified by comparing it to the absorbance of standards of known concentration. An assumption is made that the standard has an aliphatic-to-aromatic ratio and IR response similar to that of the sample. Consequently, it is important to use a calibration standard as similar to the type of contamination as possible. EPA Method 418.1 specifies a calibration mixture of 15:15:10 *n*-hexadecane: isooctane: chlorobenzene.

Example Methods

The IR-TPH method that has been most frequently used is EPA Method 418.1 (EPA-600/4-79-020 Methods for Chemical Analysis of Water and Wastes). The method is appropriate only for water samples. A separatory funnel liquid/liquid extraction technique is used to extract the hydrocarbons from the water. *Standard Methods for the Examination of Water and Wastewater*, 17th Ed., 1989, lists in Method 5520D a Soxhlet extraction technique for sludges. This extraction is frequently used to adapt Method 418.1 to soil samples. Both EPA and *Standard Methods* specify Freon 113 as the solvent of choice. At one time, the EPA issued a proposed Method 9073, an IR-based method with a Soxhlet extraction step suitable for sediment and soil. This method was not included in update III of EPA SW-846, 3rd edition. The EPA did issue Method 3560, an IR-based supercritical fluid extraction method for diesel range contamination, which may become more popular as the extraction technique gains maturity.

Method 418.1 results should not be expected to match extractable-range GC results if the hydrocarbons being measured by IR have a wider boiling range than those specified for the extractable TPH measurement. Method 418.1 is not limited by carbon range, and will detect heavier hydrocarbons than GC-based TPH analyses can measure. Furthermore, a positive bias has been reported for 418.1 vs. 8015M (GC-based) measurements in weathered limestones, silts, and clays caused by ultra-fine particles in the extract (Thomey et al., 1989).

What Do IR Methods Measure?

At a frequency of 2930 cm^{-1}, IR spectrometers measure the energy absorbance of aliphatic C-H bonds. IR-based methods can measure any extracted compounds that have alkyl groups (C-H groups) in the molecule. Any molecule that contains even one C-H bond will contribute to the measurement.

Compounds have different IR responses. Single frequency IR methods will measure straight chain paraffins, cycloalkanes, alkenes (IR response is lessened), substituted aromatics (IR response is lessened), PAHs if they have alkyl groups on them, and oxygenated molecules - ethers and alcohols (IR response is lessened). IR-based methods using a single 2930 cm^{-1} frequency will not adequately measure benzene or naphthalene because they do not contain alkyl groups, but only aromatic C-H bonds.

Interferences/Limitations

Similar to GC-based TPH methods, IR-based TPH data must be interpreted after considering certain limitations and interferences that can affect data quality. For example, not all laboratories measure the C-H absorbance exactly the same way. Within the set of methods that specify a single IR measurement, some methods call for the measurement at precisely 2930 cm^{-1} while others, including EPA Method 418.1, call for the measurement at the absorbance maximum nearest 2930 cm^{-1}. This variation can make a significant difference in the magnitude of the TPH result, and can lead to confusion when comparing duplicate sample results from laboratories that do not use the same protocol. If only C-H absorbance is measured, IR-based TPH methods will potentially underestimate TPH concentrations in samples that contain petroleum constituents such as benzene and naphthalene that do not contain alkyl C-H groups.

Because a TPH result is calculated as if the aromatics in the sample were present in the same ratio as in the calibration standard, accuracy depends upon use of a calibration standard as similar to the type of contamination as possible. Use of a dissimilar standard will tend to create a positive bias in highly aliphatic samples and a negative bias in highly aromatic samples. P.C. Hayes et.al. report that the standard Method 418.1 calibration mix will give higher results for diesel (predominantly aliphatic) than for gasoline (up to 50% aromatic). Some states use the same hydrocarbon or hydrocarbon type, rather than the specified Method 418.1 mixture, as a calibration standard.

IR methods are also prone to interferences (positive bias) from nonpetroleum sources. As shown in Figure 6, most organic compounds have some type of alkyl group associated with them whether petroleum-derived or not.

5.3 GRAVIMETRIC TPH METHODS

Gravimetric methods measure anything extractable by a solvent, not removed during solvent evaporation, and capable of being weighed. Some gravimetric methods include a cleanup step to remove biogenic material. Those that do are considered TPH methods. Those that do not are considered oil and grease (O&G) methods.

The advantage of gravimetric methods is that they are simple, quick, and inexpensive. Detection limits are approximately 5-10 mg/L in water and 50 mg/kg in soils. These methods are not especially suitable for measurement of light hydrocarbons that volatilize at temperatures below 70-85°C. They are recommended for TPH measurement only for very oily sludges, for samples containing heavy molecular weight hydrocarbons, or for aqueous samples when hexane is preferred as the solvent.

Gravimetric methods give no information on the type of fuel present, no information about the presence or absence of toxic compounds, and no specific information about potential risk associated with the contamination.

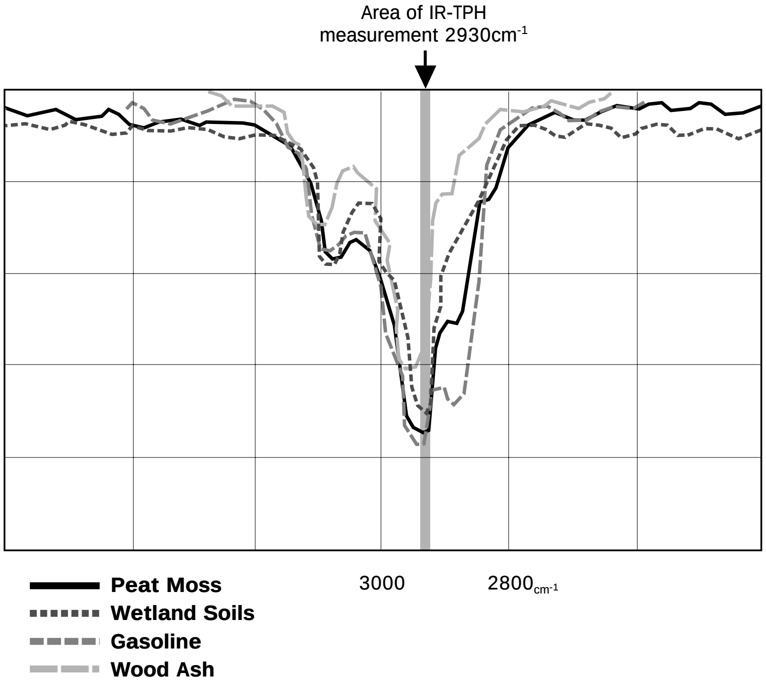


Figure 6. Infrared Spectra from Petroleum and Nonpetroleum Sources.

Overview of the Technique

TPH compounds are extracted into a suitable solvent. Biogenic polar materials typically may be partially or completely removed with silica gel. The solvent is evaporated and the residue is weighed. This quantity is called TPH or O&G and is reported as a percent of the total soil sample dry weight. These methods are better suited for heavy oils because they include an evaporation step.

Example Methods

There are a variety of gravimetric oil and grease methods suitable for testing water and soil samples. These methods have been commonly used for National Pollutant Discharge Elimination System (NPDES) permit measurements under the Clean Water Act (e.g., EPA SW-846 9070 Total Recoverable Oil and Grease; EPA 413.1 Oil and Grease, Total Recoverable).

One gravimetric method, EPA Method 9071, is recommended for measuring TPH in oily sludges. Technically the result is an oil and grease result because no cleanup step is used. "Method 9071 is used to recover low levels of oil and grease by chemically drying a wet sludge sample and then extracting it using Soxhlet apparatus. Results are reported on a dry-weight basis. Method 9071 is used when relatively polar heavy petroleum fractions are present, or when the levels of non-volatile greases challenge the solubility limit of the solvent. Specifically, Method 9071 is suitable for biological lipids, mineral hydrocarbons, and some industrial wastewaters." (EPA SW-846, Method 9071)

The EPA proposed Method 1664 as a "method for determination of n-hexane extractable material… that is not adsorbed by silica gel in surface and saline waters and industrial and domestic aqueous wastes (EPA, 1994)." This method provides for the incorporation of a cleanup step. It has been designed to replace methods based on Freon 113.

What Do Gravimetric Methods Measure?

Gravimetric "oil and grease" methods such as EPA SW-846 9071 measure anything that dissolves in the solvent and remains after solvent evaporation. These substances include hydrocarbons, vegetable oils, animal fats, waxes, soaps, greases and related biogenic material. Gravimetric TPH methods, such as proposed EPA Method 1664, measure anything that dissolves in the solvent and remains after silica gel treatment and solvent evaporation. All gravimetric methods measure any suspended solids that are not filtered from solution, including bacterial degradation products and clay fines. Method 9071 specifies using cotton or glass wool as a filter. Proposed EPA Method 1664 suggests using a 0.45-micron filter that removes suspended solids.

Interferences/Limitations

Because extracts are heated to remove solvent, these methods are not suitable for measurement of light hydrocarbons (i.e. less than C_{15}) that volatilize at temperatures below 70-85°C. Petroleum fuels, from gasoline through #2 fuel oils, are partially lost in the solvent removal operation. In addition, soil results that are reported on a dry-weight basis suffer from potential losses of light hydrocarbons during moisture determination where the matrix is dried at approximately 103-105°C for several hours in an oven.

Proposed Method 1664 uses n-hexane as a solvent. Hexane is not a good solvent for high molecular weight petroleum compounds. In theory, proposed Method 1664 should yield lower results than TPH methods using Freon or chlorinated solvents for samples contaminated with heavy oils. In practice, proposed Method 1664 has yielded results that are sometimes lower and sometimes higher than duplicate Freon-extracted samples, suggesting that extraction efficiency depends upon a variety of factors, not just solvent type.

Method 9071 currently uses Freon 113 as a solvent, but replacement solvents are needed as Freon 113 use is terminated. Replacement solvents are limited only by their ability to evaporate on a water bath at 70°C.

5.4 IMMUNOASSAY TPH METHODS

Immunoassay methods correlate TPH with the response of antibodies to specific petroleum components. A number of different testing kits based on immunoassay technology are available for rapid determination of TPH. The kits are self-contained portable systems designed to conduct analytical work in the field. They include components for sample preparation, instrumentation to read assay results, and immunoassay reagents. Currently, most of these methods measure only aromatics.

Immunoassay is used as a screening technique because its precision and accuracy are lower than standard laboratory methods such as GC/FID or IR. Immunoassay measurements may be reported as a range or a single value. Typical detection limits for TPH range from 10-500 mg/kg in soil and 200 to 500 µg/L in water.

Overview of the Technique

Antibodies are made of proteins that recognize and bind with foreign substances (antigens) that invade host animals. Synthetic antibodies have been developed to complex with petroleum constituents. The antibodies in the test kit are immobilized on the walls of a special cell or filter membrane. Water samples are added directly to the cell while soils must be extracted before analysis. A known amount of labeled analyte is added after the sample. The label is typically an enzyme with an affinity for the antibody. The sample analytes compete with the enzyme-labeled analytes for sites on the antibodies. After equilibrium is established, the cell is washed to remove any unreacted sample or labeled enzyme. Color development reagents that react with the labeled enzyme are added. A solution that stops color development is added at a specified time, and the optical density (color intensity) is measured. Because the coloring agent reacts with the labeled enzyme, samples with high optical density contain low concentrations of analytes. Concentration is inversely proportional to optical density.

Example Methods

Test kits are available for TPH, BTEX, and PAH analysis (see discussion of immunoassays in Section 6). The EPA included Method 4030, Petroleum Hydrocarbons by Immunoassay, in Update III of SW-846.

What Do Immunoassay Methods Measure?

The antibodies used in immunoassay kits are generally designed to bond with selected compounds such as BTEX and PAHs. A correction factor supplied by the manufacturer must be used to calculate the TPH concentration. The correction factor can vary depending on product type because it attempts to correlate total TPH with the measured surrogates.

Interferences/Limitations

Immunoassay tests do not identify specific fuel types. They are best used as screening tools.

Immunoassay tests are dependent on soil type and homogeneity. In particular, for clay and other cohesive soils, the tests are limited by a low capacity to extract hydrocarbons from the sample.

6. PETROLEUM GROUP TYPE MEASUREMENT: DETAILED REVIEW OF SELECTED ANALYTICAL METHODS

This section describes group-type methods for petroleum hydrocarbons. Group-type methods are designed to separate hydrocarbons into categories, such as saturates, aromatics, and polars/resins, or “PIANO” - paraffins, isoparaffins, naphthenes, olefins, and aromatics. These High Performance Liquid Chromatography (HPLC) and GC methods were typically developed for monitoring refinery processes or evaluating organic synthesis products, although they are beginning to be used for environmental applications. Column chromatographic methods that separate saturates from aromatics are often used as preparative steps for further analysis by GC/MS. Thin layer chromatography is sometimes used as a screening technique for petroleum product identification.

6.1 THIN LAYER CHROMATOGRAPHY (TLC) GROUP TYPE METHODS

TLC is perhaps an underutilized test method in the environmental field. Organic chemists sometimes use TLC to determine which stationary and mobile phases provide the best separations. The same stationary and mobile phases may then be used for more sophisticated HPLC analysis.

In the environmental field, TLC is best used for screening analyses and characterization of semivolatile and nonvolatile petroleum products. Precision and accuracy of the technique is inferior to Method 8015 or 418.1 analysis, but when speed and simplicity are desired, TLC may be a suitable alternative. For characterizations of heavy petroleum products such as tar or asphalt, TLC has the advantage of separating compounds that are too heavy to pass through a GC. While TLC does not have the resolving power of a GC, it is able to separate different classes of compounds.

Overview of the Technique

Thin layer chromatography analysis is fairly simple. Since TLC does not give highly accurate or precise results, there is no need to perform the highest quality extractions. Soils are easily extracted by shaking or vortexing with solvent. Water samples are extracted by shaking in a separatory funnel. If one suspects that interfering compounds are present, silica gel can be added to clean the extract.

Sample extract aliquots are placed close to the bottom of a glass plate coated with a stationary phase. The most widely used stationary phases are made of an organic hydrocarbon moiety bonded to a silica backbone. For the analysis of petroleum hydrocarbons, a moderately polar material stationary phase works well.

The plate is placed in a sealed chamber with a solvent (mobile phase). The solvent travels up the plate carrying compounds present in the sample. The distance a compound travels is a function of the affinity of the compound to the stationary phase relative to the mobile phase. Compounds with chemical structures and polarities similar to the solvent travel well in the mobile phase. For example, the saturated hydrocarbons seen in diesel fuel travel readily up a TLC plate in a hexane mobile phase. Polar compounds such as ketones or alcohols travel a smaller distance in hexane than saturated hydrocarbons.

After a TLC plate has been exposed to the mobile phase solvent for the required time, the compounds present can be viewed by several methods. Polynuclear aromatic compounds (PAHs), other compounds with conjugated systems, and compounds containing heteroatoms (nitrogen, oxygen, or sulfur) can be viewed with longwave and shortwave UV light. The unaided eye can see other material. Also, plates can be developed in iodine. Iodine has an affinity for most petroleum compounds, including the saturated hydrocarbons, and stains the compounds a reddish/brown color. Schematic examples of different products analyzed by TLC are shown in Figure 7.

Example Methods

There is no current EPA Method using a TLC technique. The TLC approach is considered to be a qualitative but useful tool for rapid sample screening.

What Do TLC Methods Measure?

TLC methods are usually qualitative. The analyst identifies the product present in a sample by comparison with concurrently run standards of different petroleum products. If the type of contamination is known, standards of known concentration can be run alongside the sample to allow visual approximation of concentration. An instrument called a densitometer can be used to measure sample concentration, but this approach removes two attractive features of TLC: cost and simplicity.

Interferences/Limitations

Limitations of TLC center on its moderate reproducibility, detection limits, and resolving capabilities. Variability between operators can be as high as 30%. Detection limits (without any concentration of the sample extract) are near 50

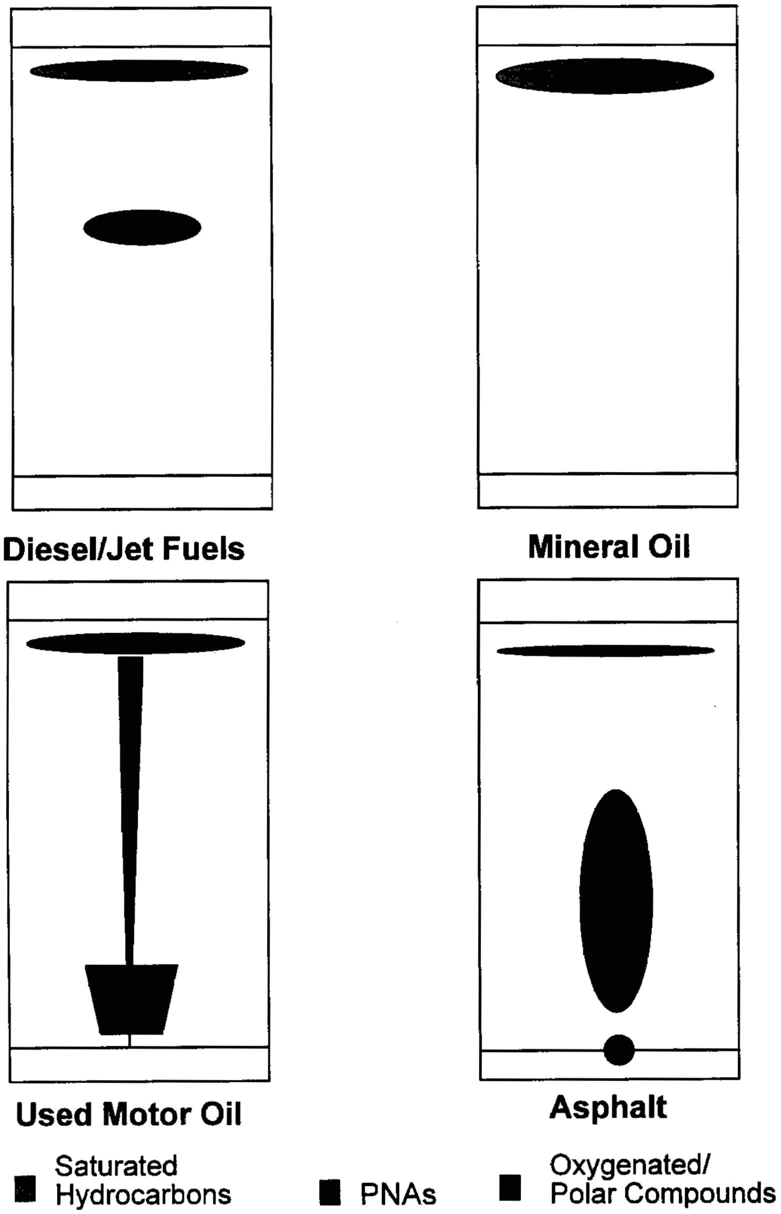


Figure 7. Schematic TLC Plates of Petroleum Products (Plates Developed in Hexane).

ppm (mg/kg) for most petroleum products in soils. When the aromatic content of a material is high, as with bunker C, the detection limit can be near 100 ppm. It is often not possible to distinguish between similar products such as diesel and jet fuel. As with all chemical analyses, quality assurance tests should be run to verify the accuracy and precision of the method.

6.2 IMMUNOASSAY GROUP TYPE METHODS

A number of different testing kits based on immunoassay technology are available for rapid field determination of certain groups of compounds such as BTEX or PAHs. These immunoassay screening kits are self-contained portable field kits that include components for sample preparation, instrumentation to read assay results, and immunoassay reagents.

Immunoassay is used as a screening technique because its precision and accuracy is lower than standard laboratory methods such as GC/FID or IR. Typical detection limits for BTEX are 2 mg/kg in soil and 200 µg/L in water. Typical detection limits for PAHs are 1 mg/kg in soil and 10 µg/L in water.

Overview of the Technique

The immunoassay technique has been previously discussed (see Section 5.4). Briefly, immunoassay tests measure TPH through the binding of petroleum constituents to protein antibodies.

Example Methods

Test kits are available for BTEX, PAH and TPH measurement. The EPA has included Method 4035, Polycyclic Aromatic Hydrocarbons by Immunoassay, in Update III of SW-846.

What Do Immunoassay Methods Measure?

The antibodies used in immunoassay kits are designed to bond with specific compounds such as monaromatics, (e.g., BTEX), and PAHs.

Interferences/Limitations

Immunoassay kits may display strong biases. Most of the BTEX kits have a low affinity for benzene relative to toluene, ethylbenzene, xylenes, and other aromatic compounds. The kits with low benzene affinity underestimate the actual benzene levels. Since benzene is often the dominant compound in leachates due to its high solubility, a low sensitivity for benzene is undesirable. Benzene-specific kits are being developed. In general, test kit specificity varies by manufacturer.

The quality of PAH analysis is often dependent on the extraction efficiency. Clay and other cohesive soils lower the ability to extract PAHs. Another potential problem with PAH analysis is that the test kits may have different responses for different PAH compounds.

In addition, the target compound test kits are often subject to false positives because the antibodies have some affinity for nontarget compounds. In general, test kits give less than 25% false positives and less than 5% false negatives.

7. INDIVIDUAL PETROLEUM CONSTITUENT MEASUREMENT: DETAILED REVIEW OF SELECTED ANALYTICAL METHODS

Many common environmental methods measure individual petroleum constituents or “target compounds” rather than the whole TPH signal. Each method measures a suite of compounds selected because of their toxicity and common use in industry. For organic compounds, the EPA has generated three series of target compound methods:

- EPA 500 series, “Organic Compounds in Drinking Water,” as regulated under the Safe Drinking Water Act.
- EPA 600 series, “Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater,” as regulated under the Clean Water Act.
- EPA SW-846 series, “Test Methods for Evaluating Solid Waste: Physical/Chemical Methods,” as promulgated by the USEPA, Office of Solid Waste and Emergency Response.

The 500 and 600 series methods provide parameters and conditions for the analysis of drinking water and wastewater, respectively. EPA SW-846 is geared toward the analysis of nearly all matrices including industrial wastes, soils, sludges, sediments, and water miscible and nonwater miscible wastes. It also provides for the analysis of groundwater and wastewater but is not used to evaluate compliance of public drinking water systems. Many of these EPA methods are capable of detecting the same target analytes; however, they often differ in applicability, sample preparation, instrument operating conditions, quality assurance calibration requirements, method detection limits, quality control measures, and reporting requirements. Selection of one method over another is often dictated by the nature of the sample and the particular compliance or cleanup program for which the sample is being analyzed. It is essential to recognize that capabilities and requirements vary between methods when requesting any analytical method or suite of methods.

Table 5 lists the most common EPA methods used to detect and measure constituents of petroleum hydrocarbons. For some of the methods, additional target compounds not specified in the method may be added upon validation. Since it is not possible to list every method or identify method requirements and components in a “method comparison,” the reader is advised to refer to the appropriate EPA series or method for more information or to consult with an analytical laboratory manager for additional guidance.

Most compound-specific methods use a GC/selective detector, HPLC, or GC/MS technique. GC and HPLC techniques identify analytes based on their retention times and can be subject to interferences. For this reason, these techniques involve use of selective detectors. GC techniques typically require second-column confirmation. GC/MS provides confirmation of the identity of an analyte through its retention time and unique spectral pattern.

TABLE 5. Cross Reference to USEPA Target Analyte Methods

USEPA Series/Methods ⟶	**500 Series**		**600 Series**				**SW-846 Methods**							
Target Analytes ↓	**502.2**	**524.2**	**602**	**610**	**624**	**625**	**8015**	**8020**	**8021**	**8100**	**8240**	**8260**	**8270**	**8310**
Acenaphthene				•		•				•			•	•
Acenaphthylene				•		•				•			•	•
Anthracene				•		•				•			•	•
Benzene	•	•	•		•		•	•	•		•	•		
Benz(a)anthracene				•		•				•			•	•
Benzo(a)pyrene				•		•				•			•	•
Benzo(b)fluoranthene				•		•				•			•	•
Benzo(ghi)perylene				•		•				•			•	•
Benzo(j)fluoranthene										•				
Benzo(k)fluoranthene				•		•				•			•	•
Chrysene				•		•				•			•	•
Dibenz(a,h)anthracene										•				
Dibenz(a,h)acridine										•				
Dibenz(a,j)acridine										•			•	
7H-Dibenzo•c,g)carbazole										•				
Dibenzo•a,h)anthracene				•		•				•			•	•
Dibenzo•a,e)pyrene										•			•	
Dibenzo•a,h)pyrene										•				
Dibenzo•a,i)pyrene										•				
7,12-Dimethylbenz•a)anthracene													•	
Ethylbenzene	•	•	•		•		◆	•	•		•	•		
Fluoranthene				•		•				•			•	•
Fluorene				•		•				•			•	•
Indeno•1,2,3-cd)pyrene				•		•				•			•	•
3-Methylcholanthrene										•			•	

TABLE 5. (Continued)

USEPA Series/Methods ⟶	500 Series		600 Series				SW-846 Methods							
Target Analytes ↓	502.2	524.2	602	610	624	625	8015	8020	8021	8100	8240	8260	8270	8310
2-Methylnaphthalene													•	
Methyl-t-butyl ether •MTBE)		•						•						
Naphthalene	•	•		•		•			•	•		•	•	•
Phenanthrene				•		•				•			•	•
Propylbenzene	•	•								•				
Pyrene				•		•							•	•
Styrene	•								•		•	•		
1,2,4-Trimethylbenzene	•	•							•			•		
1,3,5-Trimethylbenzene	•	•							•			•		
Toluene	•	•	•		•		◆	•	•		•	•		
o-Xylene	•	•	◆		◆		◆	•	•		•	•		
m-Xylene	•	•	◆		◆		◆	•	•		•	•		
p-Xylene	•	•	◆		◆		◆	•	•		•	•		

• = Compounds specified in the method.
◆ = Compounds not specified in the method, but may be target compounds under the methodís general or modified.

Compound-specific methods frequently require samples to be diluted to keep the most concentrated analytes within the calibration range, or to protect the detectors from difficult-to-remove contamination. These requirements often cause low concentration analytes to fall below detection limits. Remedies for this problem may include analyzing the sample at more than one concentration or choosing a detection method with a wider dynamic range. In some cases, the detection limit problem cannot be resolved without risking potential contamination of the instrumentation.

7.1 GAS CHROMATOGRAPHY WITH PHOTOIONIZATION DETECTION (GC/PID) PETROLEUM CONSTITUENT METHODS

The photoionization detector (PID) can be tuned to be selective to aromatics. The advantage of GC/PID is its selectivity and sensitivity. Typical detection limits for light aromatics are 0.5 µg/L in water and 5 µg/kg in soil.

In some method variations, the GC is equipped with two detectors in series. A PID is used to measure benzene, toluene, ethylbenzene, and the xylenes (BTEX), while an FID measures the total TPH signal (which includes the BTEX compounds).

Overview of Technique

For volatiles, the gas chromatograph is generally interfaced with a purge and trap system as described in the section on GC-Based Methods. The photoionization detector works by bombarding compounds with ultraviolet (UV) light, generating a current of ions. Compounds with double carbon bonds, conjugated systems (multiple carbon double bonds arranged in a specific manner), and aromatic rings are easily ionized with the UV light generated by the PID lamp, while most saturated compounds require higher energy radiation.

Example Methods

EPA Method 8020 targets volatile aromatics. This method is often referred to as BTEX analysis, though the method includes other volatile aromatics in addition to BTEX. The method is similar to most volatile organic GC methods. Sample preparation and introduction is typically by EPA Method 5030 (Purge and Trap Analysis).

What Do GC/PID Methods Measure?

A PID measures volatile aromatic compounds, such as benzene, toluene, ethylbenzene and the xylenes. Some oxygenates such as methyl-t-butyl ether (MTBE) are detected. Additionally, many olefins and some branched alkanes and cycloalkanes are detected.

Interferences/Limitations

In all GC analyses, compounds are identified by the retention time of the analyte. Although the selectivity of the PID helps to minimize false positives, GC columns must be selected carefully to minimize potential interferences. Second column/second detector confirmation should be used to increase reliability of identification. In highly contaminated samples where the PID is responding to large amounts of material, running a volatile GC/MS analysis (EPA Method 8240 or 8260) for confirmation can be beneficial.

Certain false positives are common with EPA Method 8020. Trimethylbenzenes, and gasoline constituents are frequently identified as chlorobenzenes by Methods 602 and 8020 because these compounds elute with nearly the same retention times from nonpolar columns. Cyclohexane is often mistaken for benzene by combined Method 8015/8020 analyses, because both compounds are detected by a 10.2 eV PID detector and have nearly the same elution time from a Method 8015 nonpolar column. The two compounds have very different retention times on a more polar column like the type specified by the Method 8020, but a more polar column skews the carbon ranges measured by Method 8015. False positives for oxygenates in gasoline are common, especially in highly contaminated samples.

Samples containing distillate and heavier hydrocarbons are generally not analyzed by GC/PID. The PID detector is easily contaminated and desensitized by the heavier compounds.

7.2 GAS CHROMATOGRAPHY WITH FLAME IONIZATION DETECTION (GC/FID) PETROLEUM CONSTITUENT METHODS

The flame ionization detector (FID) is a nonselective detector that employs a hydrogen-fueled flame to ionize organic compounds. The advantage of GC/FID is its sensitivity to a broad range of hydrocarbon compounds. GC/FID systems are sometimes used to measure PAHs, and typical detection limits for PAHs are 10 µg/L in water and 330 µg/kg in soil.

Flame ionization detectors are destructive detection systems because the analyte is combusted during detection. They may only be used as the second detector in cases where a GC is equipped with two detectors in series. In some methods, an FID may be used to measure the total TPH signal (as in a modified EPA Method 8015) after a PID has been used to measure light aromatics such as benzene, toluene, ethylbenzene, and the xylenes (BTEX).

Overview of Technique

For semivolatiles, the gas chromatograph is generally equipped with either a packed or capillary column. Either neat or diluted organic liquids can be analyzed via direct injection, and compounds are separated during movement down the column.

The FID uses a hydrogen-fueled flame to ionize compounds that reach the detector. Any compound that burns can be detected by an FID. Ionized molecules produce a current proportional to the total volatile organic vapor concentration in the sample, and this current change is recorded as a signal. Calibration standards can be used to quantify instrument response, and analyte signals can thus be converted to concentrations.

Example Methods

EPA Method 8100 targets PAHs. Injection of sample extracts directly onto the column is the preferred method for sample introduction for this packed-column

GC technique. Detection limits for PAHs are not specified in the method, but quality control acceptance criteria values range from 5-100 µg/L.

What Do GC/FID Methods Measure?

A GC/FID system can be used for the separation and detection of nonpolar organic compounds. Semivolatiles such as PAHs are among the analytes that can be readily resolved and detected using a GC/FID system. If a packed GC column is used, four pairs of compounds may not be adequately resolved and are reported as a quantitative sum: anthracene and phenanthrene, chrysene and benzo(a)anthracene, benzo(b)fluoranthene and benzo(k)fluoranthene, and dibenzo(a,h)anthracene and indeno(1,2,3-cd)pyrene. This problem can be addressed through the use of a capillary column in place of a packed column. An FID can also detect various interfering compounds, including sulfur compounds. Other co-extracted compounds such as phthalates, which are common environmental contaminants due to their use in plastics, can also interfere with PAH analysis by GC/FID.

Interferences/Limitations

In all GC analyses, compounds are identified by the retention time of the analyte. Therefore, GC columns must be selected carefully to minimize potential interferences. FIDs are nonselective detectors and thus are sensitive to interfering compounds as well as analytes. Interferences can hide analyte signals and thus necessitate a sample cleanup step for proper quantification and identification of analytes using GC/FID.

Second column/second detector confirmation should be used to increase reliability of identification. In highly contaminated samples where the FID is responding to large amounts of material, running a semivolatile GC/MS analysis for confirmation can be beneficial.

7.3 HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC) PETROLEUM CONSTITUENT METHODS

An HPLC system is used to measure concentrations of target semivolatile and nonvolatile petroleum constituents. Unlike GC systems that require complete volatilization of the sample so that it can then pass into the chromatograph, LC systems only require that the sample be dissolved in a solvent compatible with those used in the separation. The HPLC detector most often used in petroleum environmental analysis is the fluorescence detector. These detectors are particularly sensitive to aromatic molecules, especially the PAHs. A UV detector may be used to measure compounds which do not fluoresce.

Method detection limits for PAHs by HPLC, EPA Method 8310, range from 0.013-2.3 µg/L.

Overview of Technique

PAHs are extracted from the sample matrix with a suitable solvent, which is then injected into the HPLC. Usually the extract must be filtered because fine particulate matter can collect on the inlet frit of the HPLC column, resulting in high back-pressures and eventual plugging of the column. For most hydrocarbon analyses, reverse phase HPLC (i.e., using a nonpolar column packing with a more polar mobile phase) is used. The most common bonded phase is the octadecyl or C_{18} phase. The mobile phase is commonly aqueous mixtures of either acetonitrile or methanol.

After the chromatographic separation, the analytes flow through the cell of the detector. A fluorescence detector shines light of a particular wavelength (the excitation wavelength) into the cell. Fluorescent compounds absorb light and reemit light of other, higher wavelengths (emission wavelengths). The emission wavelengths of a molecule are mainly determined by its structure. For PAHs, the emission wavelengths are mainly determined by the arrangement of the rings and vary greatly between isomers. Some EPA methods specify the use of a filter-based detector, which measures all light above a certain wavelength. Many modern detectors can tune excitation and emission wavelengths to maximize sensitivity and / or selectivity for each analyte during a chromatographic run. At the very low concentrations often found in environmental samples, fluorescence detection is linear and requires the usual generation of calibration curves. Compounds are identified based on their retention times.

A UV (ultraviolet) detector may be used for compounds like acenaphthylene, which does not fluoresce. This detector measures the absorbance of ultraviolet light by the analyte, although it is less sensitive than the fluorescence detector.

Example Methods

EPA Method 8310 targets 16 PAHs. Some of these PAHs, such as phenanthrene, pyrene, and benzo(g,h,i)perylene, are commonly seen in products boiling in the middle to heavy distillate range. The method uses an octadecyl column and an aqueous acetonitrile mobile phase. Analytes are excited at 280 nm and detected at emission wavelengths of >389 nm. Naphthalene, acenaphthene, and fluorene must be detected by a less-sensitive UV detector because they emit light at wavelengths below 389 nm. Acenaphthylene is also detected by UV detector.

What Do HPLC Methods Measure?

HPLC methods using fluorescence detection will measure any compounds that elute in the appropriate retention time range and which fluoresce at the targeted emission wavelength(s). In the case of Method 8310, the excitation wavelength excites most aromatic compounds. These include the target PAHs but also many derivatized aromatics, such as alkylaromatics, phenols, anilines, and heterocyclic aromatic compounds containing the pyrrole (indole, carbazole, etc.), pyridine (quinoline, acridine, etc.), furan (benzofuran, naphthofuran, etc.), and thiophene (benzothiophene, naphthothiophene, etc.) structures. In petroleum samples, alkyl PAHs are strong interfering compounds. For example, there are five methylphenanthrenes and over 20 dimethylphenanthrenes. The alkyl substitution does not significantly affect either the wavelengths or intensity of the phenanthrene fluorescence. For a very long time after the retention time of phenanthrene, the alkylphenanthrenes will interfere, affecting the measurements of all later-eluting target PAHs.

Interferences/Limitations

Interfering compounds will vary considerably from source to source. Samples may require a variety of cleanup steps to reach required method detection limits.

The emission wavelengths used by Method 8310 are not optimal for sensitivity of the small ring compounds. With modern electronically-controlled monochromators, wavelength programs can be used which tune excitation and emission wavelengths to maximize sensitivity and/or selectivity for a specific analyte in its retention time window.

7.4 GAS CHROMATOGRAPHY WITH MASS SPECTROMETRY DETECTION (GC/MS) PETROLEUM CONSTITUENT METHODS

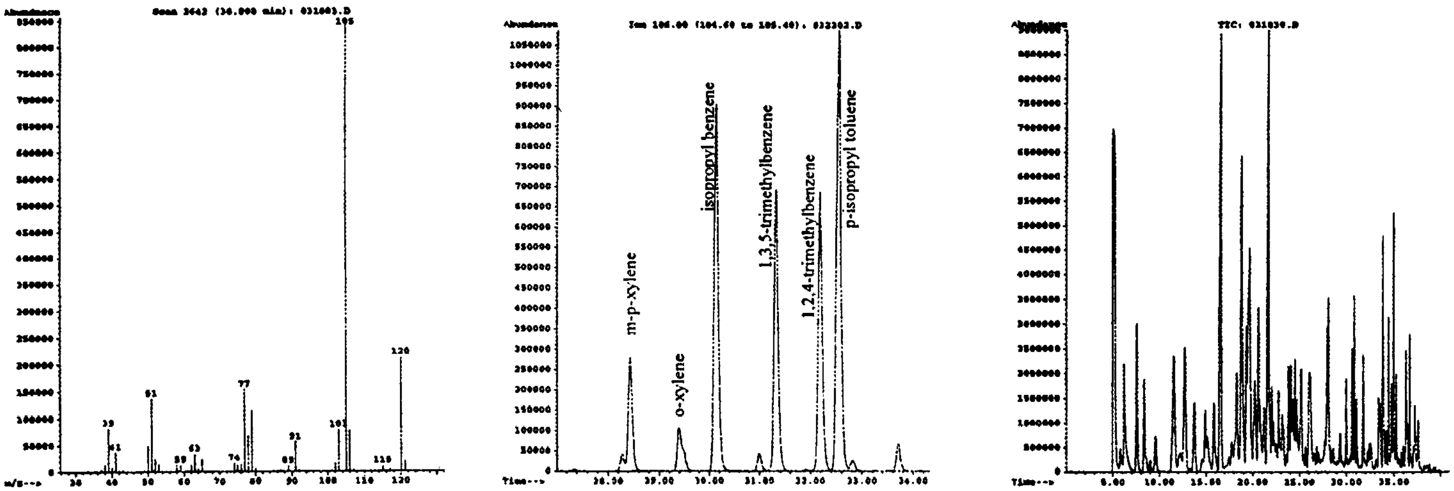
A GC/MS system is used to measure concentrations of target volatile and semivolatile petroleum constituents. It is not typically used to measure TPH. The advantage of GC/MS is the high selectivity, or ability to confirm compound identity through retention time and unique spectral pattern. Because of the complexity of their operation and of the interpretation of their output, GC/MS techniques tend to be more costly than other GC techniques (GC/PID, GC/FID).

For volatile analytes, detection limits are as low as 1-5 µg/L for water and 20 µg/kg for soil. For semivolatile analytes, detection limits are as low as 5 µg/L for water and 50 µg/kg for soil. A low-level volatiles method for soil is available, and 5 µg/kg detection limits can sometimes be achieved.

Overview of Technique

Mass spectrometer systems are designed to ionize compounds and scan for ions of specific mass-to-charge ratios. Each compound breaks apart into a consistent, recognizable pattern of fragment ions. Ideally, coupling a gas chromatograph (GC) with a mass spectrometer (MS) allows one to separate a mixture into its constituents, ionize each constituent in turn, and identify the constituent compounds by their fragmentation patterns.

Typical GC/MS outputs are shown in Figure 8. Each fragment ion is measured as a ratio of its mass to charge. A scan of all the mass-to-charge ratios done in a fraction of a second is known as a spectrum (Figure 8a). Every compound, with the exception of isomers, has a unique spectrum, although the differences may be subtle. A plot of the intensity of a single ion over time is called an ion chromatogram. Ion chromatograms can be used to identify trace concentrations of specific types of compounds in the presence of a complex mixture (Figure 8b). If all the ion responses in a scan are summed, a total ion chromatogram can be generated (Figure 8c). The total ion chromatogram of a petroleum product is similar to a GC/FID trace.



a. Mass spectrum of isopropylbenzene

b. Ion chromatogram, m/z = 105

c. Total ion chromatogram

Figure 8. Comparison of Different GC/MS Outputs.

In a technique called selected ion monitoring, or SIM, the GC/MS is set up to measure only selected target masses rather than scanning the full mass range. The output looks like Figure 8b. This technique yields lower detection limits for specific compounds. At the same time, it gives the more complete information available from the total ion chromatogram and the full-mass-range spectrum of each compound. The technique is sometimes used to quantify compounds present at very low concentrations in a complex hydrocarbon matrix. It can be used if the target compound's spectrum has a prominent fragment ion at a mass that distinguishes it from the rest of the hydrocarbon compounds.

Example Methods

The current SW-846 GC/MS method for the analysis of volatile compounds is Method 8260. A comparison with recently discontinued Method 8240 reveals that most of the compounds listed in these methods are not typically found in petroleum products. Both methods measure some petroleum compounds, including BTEX, ethylene dibromide and ethylene dichloride, which are additives associated with leaded gasolines. C_3 Benzenes, some C_4 benzenes, and napthalenes (compounds common to petroleum products) are also measured by Method 8260.

The most common method for GC/MS analysis of semivolatile compounds is EPA SW-846 8270. The 8270 list includes 16 polycyclic aromatic compounds (PAHs). Some of these PAHs are commonly seen in middle distillate to heavy petroleum products. The method also quantifies phenols and cresols, compounds that are not hydrocarbons but may occur in petroleum products. Phenols and cresols are more likely found in crude oils and weathered petroleum products.

What Do GC/MS Methods Measure?

GC/MS methods identify compounds by retention time and mass spectrum. To reduce the possibility of false positives, the intensities of one to three selected ions are compared to the intensity of a unique target ion of the same spectrum. The sample ratios are compared to the ratios of a standard. If the sample ratios fall within a certain range of the standard, and the retention time matches the standard within specifications, the analyte is considered present (Figure 8). Quantification is performed by integrating the response of the target ion only.

Interferences/Limitations

Mass spectrometers are among the most selective detectors, but they are still susceptible to interferences. Isomers have identical spectra, while many other compounds have similar mass spectra. Heavy petroleum products can contain thousands of major components that are not resolved by the gas chromatograph. As a result, multiple compounds are simultaneously entering the mass spectrometer. Different compounds may share many of the same ions, confusing the identification process. The probability of misidentification is high in complex mixtures such as petroleum products.

Sometimes, identification of compounds is accomplished by an automated library search program. Because computer libraries can never contain all possible petroleum isomers and frequently contain pesticides, plastics and other compounds not found in petroleum, they frequently misidentify compounds. Computer library identifications should only be used with extreme caution.

GC/MS is not a suitable technique for quantifying TPH. The response of an FID is proportional to the mass of hydrocarbon present and is insensitive to the type of hydrocarbon (e.g., aromatic, n-alkane and olefin). A mass spectrometer, however, may have very different responses for two different hydrocarbon compounds. Since petroleum products are complex mixtures of hydrocarbons, the same mass of two different products may have two different responses on a mass spectrometer.

8. EVOLVING METHODS FOR PETROLEUM HYDROCARBON FRACTIONS

New petroleum analytical methods are being developed and used that identify and quantify TPH as hydrocarbon fractions. Rather than quantifying a complex TPH mixture as a single number, petroleum hydrocarbon fraction methods break the TPH mixture into discrete hydrocarbon fractions, thus providing data that can be used in a risk assessment and in characterizing product type and compositional changes (e.g., weathering).

8.1 WHAT DO PETROLEUM FRACTION METHODS MEASURE?

TPH fraction methods can be used to measure both volatile and extractable hydrocarbons. The currently available TPH fraction methods, including the TPHCWG Method and the Massachusetts Department of Environmental Protection (MA DEP) EPH/VPH Method, are most appropriate for measurement of hydrocarbons in the approximate carbon range C_6 to C_{28}. Lighter and heavier hydrocarbons may have lower recoveries, but their detection is possible and may be enhanced by method modification. MA DEP was the first to use a petroleum fraction approach in characterizing and evaluating potential human health risk associated with petroleum contaminated sites. The MA DEP fractions are divided according to the expected toxicity of individual constituents. The Working Group fractions are based on the expected environmental behavior of individual petroleum constituents. This grouping simplifies the environmental modeling needed to assess potential human exposure to petroleum contamination. In both the MA DEP and Working Group approaches, petroleum constituents are first divided into aliphatic and aromatic compound fractions prior to further subdivision according to chemical class and boiling ranges.

8.2 WHY USE PETROLEUM FRACTION METHODS?

In contrast to traditional TPH methods that report a single concentration number for complex TPH mixtures, TPH fraction methods report separate concentrations for discrete aliphatic and aromatic fractions. The available petroleum fraction methods are GC-based and are thus sensitive to a broad range of hydrocarbons.

Identification and quantification of aliphatic and aromatic fractions allows one to identify petroleum products and evaluate the extent of product weathering. These fraction data also can be used in risk assessment. Together, the fractions represent the mass of petroleum used to evaluate noncancer risk. Cancer risk is evaluated separately from the fractions, using concentration data for individual carcinogenic petroleum constituents (e.g., benzene and several PAHs).

8.3 EXAMPLES OF PETROLEUM FRACTION METHODS

Several TPH fraction methods are either in development and/or are gaining regular usage. Two such methods include the TPHCWG Method and the MA DEP EPH/VPH Method. The TPHCWG Method was developed with the assistance of Shell Development Company. The Massachusetts EPH/VPH is the promulgated TPH methodology for site cleanups in Massachusetts. The transition to this method has occurred over several years, and state cleanup standards for both soil and groundwater have been developed for the measured EPH/VPH fractions. Petroleum fractions quantified in both of these methods have been paired with toxicity criteria so that human health risk associated with exposures to petroleum-contaminated media can be assessed.

TPHCWG Analytical Methodology

This method is designed to characterize C_6 to C_{28}+ petroleum hydrocarbons in soil as a series of aliphatic and aromatic carbon range fractions. The extraction methodology differs from other petroleum hydrocarbon methods because it uses *n*-pentane and not methylene chloride as the extraction solvent. If methylene chloride is used as the extraction solvent, aliphatic and aromatic compounds cannot be separated. *n*-Pentane extracts petroleum hydrocarbons in this range efficiently. The whole extract is separated into aliphatic and aromatic petroleum-derived fractions. This group-type separation is based on SW-846 EPA Method 3611 (Alumina Column Cleanup and Separation of Petroleum Wastes) and SW-846 EPA Method 3630 (Silica Gel Cleanup). The aliphatic and aromatic fractions are analyzed separately by gas chromatography, and quantified by summing the signals within a series of specified carbon ranges that represent the fate and transport fractions. The gas chromatograph is equipped with a boiling point column (non-polar capillary column). GC parameters allow the measurement of a hydrocarbon range of n-hexane (C_6) to n-octacosane (C_{28}+), a boiling point range of approximately 65 °C to 450 °C.

The analytical method exploits the relationship between petroleum hydrocarbon fate and transport properties and boiling point discussed in TPHCWG Volume 3. The method has been specifically designed to resolve and quantify the 13 aliphatic and aromatic fate and transport fractions selected by the Working Group. The Working Group also assigned toxicity criteria to each fraction by selecting toxicity data most representative of the fraction from the toxicology literature on whole products, mixtures and individual petroleum constituents. When paired with the Working Group toxicity criteria, the fate and transport fraction data can be used to assess human health risk associated with exposures to petroleum-contaminated environmental media.

The method not only separates and quantifies aliphatic and aromatic fractions, but it can also be used to obtain a TPH fingerprint for the sample. Experienced GC analysts can use the fingerprint to identify the type of petroleum release, and the extent of weathering. The method is currently written as a tiered approach with fingerprint analysis preceding characterization of aliphatic and aromatic fractions. In this way, the fingerprint can be used for a preliminary evaluation of the nature and extent of the release.

The method is versatile and performance-based; therefore, it can be modified to accommodate data quality objectives. It has been successfully applied to the characterization of neat crude oil and petroleum products as well as soils containing gasoline, JP-4, diesel and crude oil with different degrees of weathering.

Massachusetts EPH/VPH Approach

MA DEP published a regulatory framework for evaluating the TPH parameter in human health risk assessments (MA DEP, 1994; Hutcheson, 1996). This framework recommends using the EPH/VPH analytical procedure for petroleum hydrocarbon mixtures. This procedure consists of two steps; quantification of volatile petroleum hydrocarbons (VPH) and quantification of extractable petroleum hydrocarbons (EPH). The VPH method includes the following analytes: benzene, toluene, ethylbenzene, and total xylenes (BTEX) as well as naphthalene and MTBE; alkanes/cycloalkanes in the C_5 to C_8 and C_9 to C_{12} carbon ranges; and aromatics/alkenes in the C_9 to C_{10} carbon range. The EPH method includes the following analytes: polycyclic aromatic hydrocarbons (PAHs); alkanes/cycloalkanes in the C_9 to C_{18} and C_{19} to C_{36} carbon range; and aromatics/alkenes in the C_{10} to C_{22} carbon range.

For the VPH fraction, the protocol for water samples involves direct purge and trap and for soil samples involves a methanol extraction followed by purge and trap concentration. The VPH methodology calls for a PID and FID in series. GC/PID is recommended for separation and detection of the VPH target analytes and the C_9 to C_{10} aromatic fraction, and the FID is used to detect the C_5 to C_8 and C_9 to C_{12} aliphatic fractions. For the EPH fraction, the protocol for both water and soil samples involves a methylene chloride extraction followed by Kuderna-Danish concentration. After solvent exchange to hexane, a Sep-pak (silica gel) cartridge and two eluants (hexane followed by methylene chloride) are used to separate the extract into the aliphatic and aromatic fractions. GC/FID is used as the detector following concentration. Quantification of target analytes for both the VPH and EPH procedures is done by comparing the area under the chromatogram from the appropriate FID or PID response to the corresponding response of a standard mixture containing the compounds of interest.

MA DEP developed the EPH/VPH methodology for specific application in human health risk assessment. Similar to the Working Group's fate and transport fractions, MA DEP's fractions have been assigned toxicity criteria based on reference compounds selected to represent each fraction. Cleanup standards have been promulgated for the EPH/VPH fractions based on the toxicity of the reference compounds, and the state has recommended the use of either or both EPH and VPH analysis for a variety of petroleum mixtures.

APPENDIX I

Hydrocarbon Chemistry

HYDROCARBON CHEMISTRY

Petroleum and petroleum products are very complex mixtures that contain primarily hydrocarbons (compounds containing molecules of carbon and hydrogen atoms), heteroatom compounds (compounds containing molecules of carbon and hydrogen atoms with heteroatoms such as sulfur, nitrogen, or oxygen), and relatively small concentrations of metallic constituents. The complexity of petroleum and petroleum products increases with carbon number. The heavier the material, the larger the number of possible combinations of atoms. Gasoline has a smaller number of components than diesel. For example, there are only 75 combinations for molecules containing 10 carbons, but there are 366,319 possible combinations for molecules containing 20 carbons. It is impossible to identify all components, so petroleum and petroleum products are characterized in terms of boiling range and approximate carbon number.

Regardless of the complexity, petroleum compounds can be generally classified into two major component categories: hydrocarbons and nonhydrocarbons. Hydrocarbons comprise the majority of the components in most petroleum products and are the compounds that are primarily (but not always) measured as TPH. The nonhydrocarbon components (those containing sulfur, nitrogen and oxygen heteroatoms, as well as carbon and hydrogen in the molecule) are relatively minor in most refined motor fuels as they tend to concentrate in the heavy distillation fractions.

The hydrocarbon constituents can be grouped into saturated hydrocarbons, unsaturated hydrocarbons, and aromatics. There are several subclasses of importance within these groups. Figure I-1 summarizes the different categories and subclasses.

SATURATED HYDROCARBONS

Saturated hydrocarbons are the primary class of compounds found in petroleum and most petroleum products. They are comprised of single C-C bonds (with all other remaining bonds saturated with H atoms.) The molecules can be arranged in several configurations:

- **Aliphatic**: Straight or branched with the general formula:

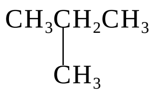
$$C_nH_{2n+2}$$

The common names for these types of compounds are alkanes and isoalkanes. The petroleum industry refers to these compounds as paraffins and isoparaffins, respectively.

Examples:

$CH_3CH_2CH_2CH_3$

Butane



$$\underset{\displaystyle CH_3}{CH_3\overset{}{C}H_2CH_3}$$

Isobutane

- **Alicyclic**: Cyclic compounds with the general formula:

$$C_nH_{2n}$$

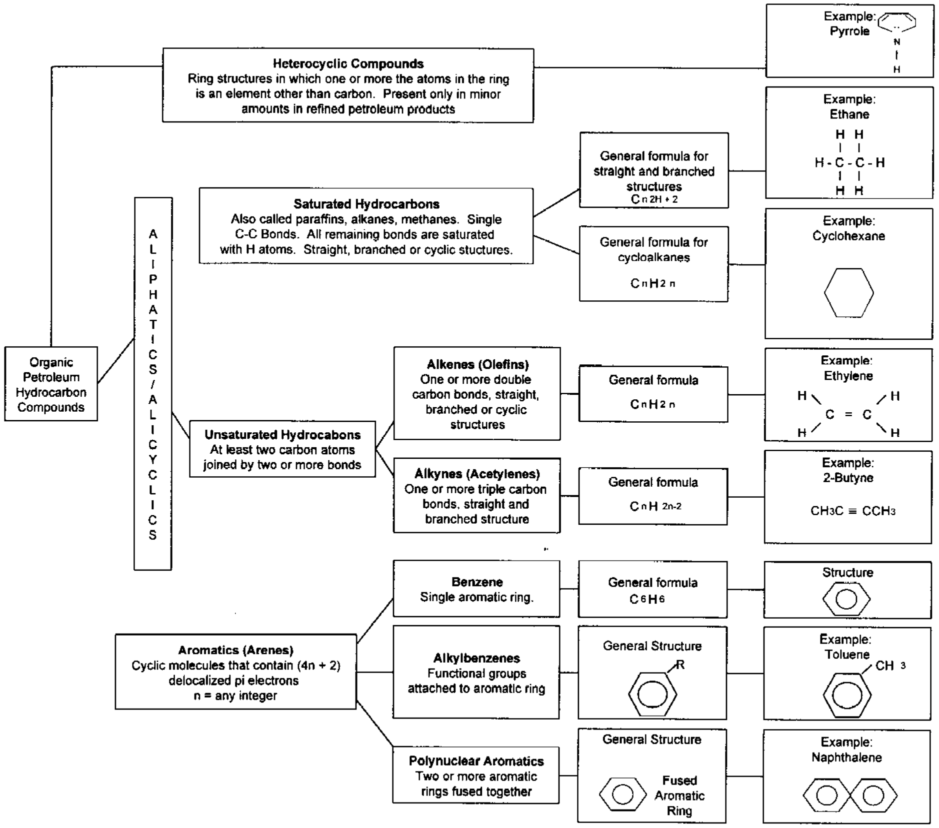
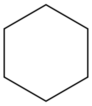


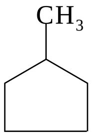
Figure I-1. TPH Compounds by Class.

These compounds are saturated hydrocarbons containing one or more rings which may also contain saturated side chains. These compounds are also called cycloalkanes. The petroleum industry commonly calls them naphthenes or cycloparaffins.

Examples:



Cyclohexane



Methylcyclopentane

UNSATURATED HYDROCARBONS

This class of compound has at least two carbon atoms in the molecule joined by two or more bonds (C=C for alkenes, or C≡C for alkynes). These classes of compounds are not found in crude oil and are produced primarily in cracking processes in the production of smaller molecules from heavier ones. As molecules crack, they may form double bonds when there is not enough hydrogen available to saturate the molecule. Gasoline, for example may contain a significant amount of double-bonded carbon.

- **Alkenes/Olefins**: These compounds can be straight chain, branched, or cyclic compounds. The general formula is:

$$C_nH_{2n}$$

Examples:

$H_2C=CH_2$ Ethylene

$H_2C=CHCH_2CH_3$ 1-Butene

- **Alkynes/Acetylenes**: These compounds are found in straight chain and branched structures. The general formula is:

$$C_nH_{2n-2}$$

Examples:

$HC\equiv CCH_3$ Acetylene

$HC\equiv CCH_2CH_3$ 1-Butyne

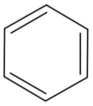
AROMATICS

Aromatic compounds are a special class of unsaturated hydrocarbons. These compounds are based on the benzene ring structure. The benzene ring contains six carbons. Each carbon in the ring binds with one hydrogen, not typically shown in structure diagrams. The benzene molecule can have one or more hydrogens substituted with side chains resulting in alkyl benzenes, or there may be two or more aromatic rings fused together resulting in polycyclic aromatic hydrocarbons (PAHs). All crudes and petroleum products (except some solvents produced from petroleum) contain aromatics.

- **Benzene**: This is a single aromatic ring with the general formula:

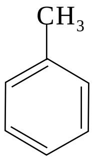
$$C_nH_n$$

Structure:

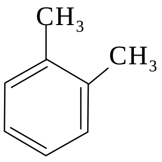


- **Alkylbenzenes**: These compounds have the base aromatic ring with side chains attached.

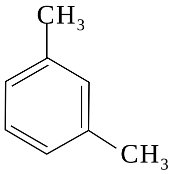
Examples:



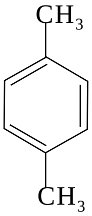
Toluene



o-Xylene



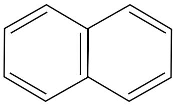
m-Xylene



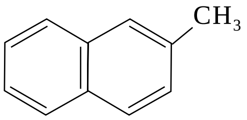
p-Xylene

- Polycyclic Aromatic Hydrocarbons (PAHs), are also known as polycyclic aromatic hydrocarbons. These compounds are two or more aromatic rings fused together.

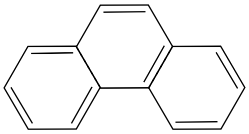
Examples:



Naphthalene



2-Methylnaphthalene



Phenanthrene

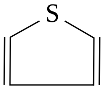
Aromatics as a class are common environmental contaminants at petroleum release sites. Monoaromatics, such as benzene, toluene, and xylenes have significant water solubility, and are mobile in the environment. BTEX are volatile target analytes in EPA methods. Several PAHs that can be found in petroleum and some petroleum products can be persistent contaminants, particularly in soil and sediment matrices. PAHs are semivolatile target analytes in EPA methods.

NONHYDROCARBON COMPOUNDS

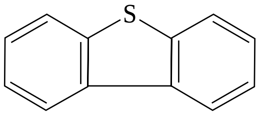
Crude oils contain significant amounts of organic nonhydrocarbon constituents, mainly sulfur, nitrogen, and oxygen-containing compounds. There are also smaller amounts of organometallic compounds and inorganic salts. These compounds are concentrated in the heavier distillation fractions and residues during refining. They are often referred to as asphaltenes.

Depending on the method used for determination of TPH, some of the sulfur, nitrogen, and oxygen-containing compounds may be included in the TPH measurements. By definition, these compounds are NOT hydrocarbons.

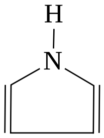
Examples:



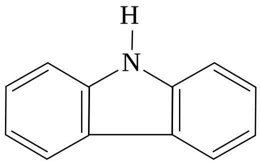
Thiophene



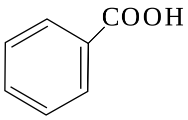
Dibenzothiophene



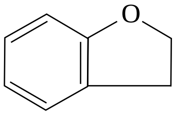
Pyrrole



Carbazole



Benzoic Acid



Benzofuran

SUMMARY

The composition of petroleum and petroleum products is extremely complex. This complexity makes it difficult to determine environmental impacts at petroleum release sites using traditional EPA methods. It should be very clear that a TPH measurement cannot be used to evaluate risk. TPH methods measure a subset of the sum of a complex mixture of compounds varying greatly in potential toxic properties. Target analyte methods measure only a few of the many compounds in petroleum. Clearly, different analytical methods used for the determination of the environmental impact of petroleum and petroleum products will provide very different information.

APPENDIX II

Characterization of Petroleum Products

APPENDIX II-A: PRODUCT COMPOSITION AND SPECIFICATION

A brief description of the most common petroleum products is included to assist in understanding the composition of these materials and in the interpretation of TPH for those cases in which the product type is known. These descriptions are only general guidelines. Actual specifications for any given product may vary depending on a variety of factors including specific refinery operations, market, season, etc.

Petroleum products are either fractions from the distillation of crude oil or blends of distillation fractions with reprocessed refinery streams. Complex refinery operations govern the blending of different streams to produce the final commercial products (See Appendix III for an illustration of how different products are refined in a typical refinery).

Refinery operations are targeted to produce products that meet set specifications. A specification is a detailed listing of requirements and their acceptance ranges. Specifications for petroleum products are performance driven. Tests ensure the product has the appropriate physical and chemical properties for the intended use. Specifications can change over time, based on regulatory pressures, evolving manufacturing requirements, and sensitivity to environmental concerns.

Three major groups write specifications for products and materials: ASME (American Society of Mechanical Engineers), ASTM (American Society for Testing and Materials), and API (American Petroleum Institute). The American Society for Testing and Materials has established specifications for most products used on a large -scale basis in this country. It has sanctioned and approved numerous standardized tests for measuring the properties established in petroleum product specifications. Other specifications are written by manufacturers, end users, and industry groups.

Petroleum products are used throughout our society from heavy military and industrial end uses to large-scale uses in numerous consumer products. Specifications required for the wide range of commercial petroleum products are varied. Boiling range distribution, elemental composition, viscosity, flash point, pour point, viscosity index, API gravity, specific gravity, color, ash content, water content, demulsibility, as well as many other factors may be part of the specifications of a particular product for a specific use or application. While a physical property such as boiling range may establish the initial product specification, other finer specifications define their ultimate use in certain applications. The more specialized the application, the more detailed the list of specifications becomes for a particular petroleum product.

GASOLINE

Automotive gasoline is a blended product. Refined to maximize cost-effectiveness, it is manufactured from the C_4 to C_{12} boiling range portions of distilled crude oil and a variety of processed refinery streams. Depending on the source, a barrel of crude oil can yield 10-40% gasoline from straight distillation. To increase yield and performance, refinery processes crack large molecules and alkylate or polymerize smaller molecules to produce molecules in the desired gasoline carbon range. Some molecules that are in the right range but burn unevenly will be reformed or isomerized to increase their octane value. Oxygenates that may be added to gasoline include methyl-tertiary butyl ether (MTBE), as well as alcohols. Gasoline contains additives which may be added in relatively small amounts to enhance certain performance characteristics.

The composition of gasoline is well characterized. It is a blended product of many refinery streams. The potential number of isomers in this carbon range is relatively small so that detailed analysis is possible. There are more than 200 individual components in the C_4 to C_{12} boiling range. These hydrocarbons include 40 to 70% straight, branched and cyclic alkanes (normal paraffins, isoparaffins, and naphthenes); alkenes (olefins) in variable concentrations but usually less than 10%; and 20 to 50% aromatics. The major components of gasoline that are targets in EPA methods are benzene, toluene, ethylbenzene, xylenes, and naphthalene. These compounds are sufficiently water soluble to leach to groundwater and are thus mobile in the environment.

Gasoline can be produced to meet certain specifications. Its use demands that the end product meet specifications for volatility, octane, boiling range distribution, sulfur content, gum content, water tolerance, corrosion resistance, and additive-derived properties. The American Society for Testing and Materials has a standard for motor gasolines, D 4814, which provides general guidelines for gasoline quality. Volatility affects drivability and adequate starting. The volatility of a motor gasoline must be such that enough low-boiling hydrocarbons are present in the cold cylinders of the engine to form a flammable mixture. Octane indicates the fuelís ability to prevent preignition or knocking in an engine. Octane ratings are assigned to motor gasolines as an indication of the antiknock properties of the fuel. Alkyl lead antiknock compounds, such as tetraethyl lead (TEL) and a manganese tricarbonyl compound (MMT), were used as octane improvers until the advent of unleaded gasolines in the mid 1970s when these additives were eventually phased out. The proper octane levels are achieved in unleaded gasolines today by the use of oxygenated additives (e.g., MTBE), higher concentrations of aromatic hydrocarbons, and higher concentrations of branched chain hydrocarbons. These molecules have high research octane numbers (RON) and motor octane numbers (MON). Octane numbers posted at gasoline dispensers are an average of the RON and the MON. Additives blended into gasolines affect their overall performance under many different conditions which exist during the operation of an automobile or other vehicle. Some of the most commonly used gasoline additives (past and present) are shown in Table II-A-1.

NAPHTHAS / SOLVENTS

Petroleum naphtha is a generic term for a variety of refined or unrefined petroleum products in the C_6 to C_{12} range. Different naphthas can be all aromatic, all paraffinic, aromatic/paraffinic combinations, or aromatic compounds such as xylenes, etc. Another common term for naphtha is mineral spirits. A commonly used type is Stoddard solvent that is typically in the C8 to C12 range. Naphthas are widely used as diluents for paints, as solvents in dry-cleaning, for cutback asphalt, and in extraction processes.

TABLE II-A-1. Common Gasoline Additives

Additive	**Composition**	**Function**
Oxidation inhibitors	Aromatic amines and phenols	Inhibit oxidation and gum formation
Corrosion inhibitors	Carboxylic acids and carboxylates	Inhibit corrosion of iron
Metal deactivators	Chelating agent	Inhibit oxidation and gum formation catalyzed by certain metals, primarily copper
Carburetor detergents	Amines and amine carboxylates	Prevent deposits in carburetor throttle body
Detergent-dispersants	Polybutene succinimides	Prevent deposits in carburetor throttle body and intake manifold and ports
Deposit control additives	Polybutene amines, polyether amines	Remove and prevent deposits throughout carburetor, intake manifold, and intake ports and valves
Oxygenated blending agents	Methyl-tert-butyl ether (MTBE), ethanol, methanol, tert-butyl alcohol (TBA)	Extend gasoline supply, increase octane number, environmental requirements, reduce CO emissions
Antiicing additives	Surfactants, alcohols, and glycols	Prevent icing in carburetor and fuel system
Dyes	Azo and other oil soluble compounds	Identification
Antiknock compounds	Lead alkyls, Organo-manganese compounds	Increase octane number
Lead scavengers	Ethylene dichloride (EDC), ethylene dibromide (EDB)	Reduce accumulation of inorganic lead deposits in the engine

Naphthas encompass a wide variety of volatile hydrocarbons with varying physical properties. The initial boiling point may be as low as 80°F; and end points may reach 450°F, depending on the application. A more narrow boiling range is specified by ASTM for aliphatic and aromatic naphthas. According to ASTM standards for naphthas in D 3734 and D 3735, there are five basic types of naphthas. Three are classified as VM&P naphthas that are primarily aliphatic in composition and classified as Type I-regular (minimum flash point of 40°F); Type II-high flash (minimum flash point of 80°F; and Type III-odorless (minimum flash point of 40°F). There are two types of high-flash aromatic naphthas: Type I, which is known as Aromatic 100, has a minimum flash point of 100°F; and Type II, which is known as Aromatic 150, has a minimum flash point of 150°F.

Specifications for naphthas include color, odor, sulfur content, aromaticity, flash point, specific gravity, initial boiling point, Kauri-butanol value, copper corrosion, bromine number, and appearance.

AVIATION GASOLINE

Aviation gasolines have strictly limited hydrocarbon compositions with the highest octane economically possible within a specific boiling range. Aviation gasolines are comprised of 50-60% saturated hydrocarbons (paraffins and isoparaffins), 20-30% cycloalkanes (naphthenes), approximately 10% aromatics, and usually no olefins. Most aviation gasolines are made by blending selected straight-run naphtha fractions with isopentane and alkylate. All aviation gasolines are leaded and use tetraethyllead (TEL) with ethylene dibromide (EDB). Table II-A-2 lists additives typically used in aviation gasoline.

There are different grades of aviation gasolines that can be distinguished by the color dye additives and the lead content. Examples of designations of aviation gasoline include Grade 80 (red), Grade 100 (green), and Grade 100LL (blue).

JET FUELS

There are two general grades of jet fuel:

- a wide-cut heavy naphtha-kerosene blend previously used by the U.S. Air Force as JP-4; and
- a kerosene used by the world's airlines as Jet A or Jet A-1, by the U.S. Navy as JP-5, and currently by the U.S. Air Force as JP-8. JP-5 is a more narrow cut of JP-8.

JP-4 is a type of aviation fuel that is currently being phased out of use in military aircraft. It is a mixture of naphtha, gasoline, and kerosene hydrocarbons. The typical carbon range includes C_6 to $C_{14\text{-}16}$.

Jet A fuels are essentially a fraction distilled from crude oil mixed with some cracked material. These products contain saturated hydrocarbons (80 to 90%), aromatics (10 to 20% for jet fuel and as high as 30% for kerosene), and do not generally contain alkenes (olefins). Sulfur compounds are removed and any alkenes are saturated by hydrotreating. Jet fuels (Jet A), like kerosenes, are primarily comprised of hydrocarbons in the C_8 to C_{17} range with the majority in the C_{10} to C_{14} range. There is no detailed analysis of the components in this range because the

TABLE II-A-2. Aircraft Fuel Additives

Additive	Composition	Function
Aviation Gasoline		
Antiknock	Lead alkyls	Increase octane number
Oxidation Inhibitor	Alkylated amines aromatic phenols	Inhibit oxidation
Dyes	Azo and other oil soluble compounds	Identification
Lead scavenger	Ethylene Dibromide	Reduce accumulation of inorganic led deposits in the engine
Jet Fuel		
Antirust	Alkyl amine salts of orthophosphoric acid, polyoxyethylated compounds, diamines and amides	Minimize formation of rust
Antiicing	Ethylene glycol monomethyl ether, glycol ethers	Prevent ice formation
Antioxidation	Alkyl phenols, arylamines	Provide oxidation stability
Antistatic	Pure paraffinic hydrocarbons, Shell's ASA addative (Chromium salt of alkylated salicylic acid, calcium disulfosucccinimide and vinyl methacrylate copolymer)	Decrease specific resistivity of the fuel to lesson the incidence of fires
Biocide	Organoboron compounds	Inhibit hte growth of bacteria and fungi in storage tanks

Source: *McGraw-Hill Encyclopedia of Science and Technology* and *Corrosion Inhibitors*, an offical NACE Publication, 1973.

product is processed to meet boiling range and performance characteristic specifications. The number of isomers in this carbon range precludes detailed identification of individual components.

All jet fuels meet stringent specifications necessary for the performance requirements of aircraft turbine engines and fuel systems. These fuels must meet specifications of extreme cleanliness, freedom from oxidation in high-temperature zones, atomization and ignition at low temperatures, fluidity at low temperatures, combustion quality, smokeless and burn with adequate heat release. In addition, jet fuel must be dry and have an extremely low freezing point. It must also contain an electrical conductivity additive to ensure rapid dissipation of charge, which can cause ignition of the product resulting in fires.

KEROSENE

Kerosene is essentially the same boiling range distillation fraction as Jet A and thus has the same hydrocarbon composition. There are some differences in specifications. Most commercial kerosenes are sold under two general classes: No. 1-K and No. 2-K. No. 1-K kerosene is a low-sulfur grade kerosene while No. 2-K is a regular grade of kerosene with a higher sulfur content. Additional specifications for kerosene include low aromatics content (except in the case of tractor fuel), low viscosity, a flash point greater than 73°F, and a melting point no more than -25°F. Kerosene with high paraffin content is used in oil lamps.

DIESEL FUEL

Transportation diesels are manufactured primarily from distilled fractions of crude oil with some blending with cracked gas oils. The major components of diesels are similar to those present in the crude oil, but include a higher fraction of aromatics (up to 30 to 40%). Diesel fuel is essentially the same as furnace oil, but the proportion of cracked gas oil is usually less than in furnace oil. Although cracking processes also produce small alkenes as well as aromatics, the small alkenes are not in the diesel carbon range and end up in the gasoline pool. The typical carbon range for diesel #1 grades is C_8 to C_{17} range, with the majority in the C_{10} to C_{14} range (similar to Jet A and kerosene). The typical carbon range for diesel # 2 fuels is C_8 to C_{26} , with the majority in the C_{10} to C_{20} range (similar to fuel oil No. 2). In all cases, the majority of the fuels is 60-90% normal, branched, and cyclic alkanes.

These middle petroleum distillates are classified primarily by the ASTM for the intended primary applications. The specifications are usually for a defined volatility, boiling range, and sulfur content. There are five different grades of diesel fuel oils for uses that range from automobiles, commercial trucks, buses, to marine and railroad engines. Additional specifications include requirements for viscosity, ash content, copper strip corrosion rating, cetane number (a measure of the ignition quality that influences starting and combustion roughness, analogous to octane number for gasoline), cetane index, cloud point, aromaticity, water and sediment content, and carbon residue. Additives are used in diesel fuels to protect the fuel system against deposits, rust and corrosion, to keep the fuel system components clean, and to improve diesel fuel cetane (Table II-A-3). Many of these specifications are outlined in ASTM D 975.

TABLE II-A-3. Typical Classes of Diesel Fuel Additives

Additive	**Composition**	**Function**
Dispersant	Succinate esters, succinimides, Mannich bases	Extend filter life, disperse particulates and sediment
Detergent	Synthetic sulfonates, phenates, salicylates, phosphonates	Prevent deposits
Antirust	Ethoxylated alkyl phenols, alkenyl succinic acids, amine phosphates	Prevent rust
Cetane Number Improver	Alkyl nitrates, hydroperoxides	Improve burning characteristics of fuel
Biocide	Organoboron compounds	Inhibit the proliferation of bacteria and fungi
Pour Point Depressant	Polymethacrylates, alkylated naphthaenes, ethylene vinyl acetate copolymers, fumarate-vinylacetate copolymers, alkylated polystyrene, acylated polystyrene, polyolefins,aliphatic amine oxides,and oxidized wax	Reduce the yield stress of the fuel and improve pumpability at low temperatures

Source: *McGraw Hill Encyclopedia of Science and Technology.*

FUEL OILS

Fractions from crude oil distillation that are heavier than diesel/middle distillates are often called residual fuel oils. Other commonly used names are No. 4, 5, and 6 fuel oils and bunker C. These oils can be used as fuel or as feed to refinery conversion units to produce lighter, more valuable fuel fractions. The sources of fuel oils may be directly from the distillation process and/or a complex process of selection and blending of various petroleum fractions to meet definite specifications. In principle, these materials start in the C_{20} to C_{25} range and can go higher than C_{40}. Blending with lower molecular weight fractions to decrease viscosity of heavier fractions may widen the carbon range to as low as C_6. The composition of these oils is quite variable but they all contain saturated and aromatic hydrocarbons (including PAHs) as well as nonhydrocarbons (heteroatom containing molecules).

There are seven different grades of fuel oil which are primarily used in different types of fuel burning equipment under different conditions of operation. They are grades 1& 2, grades 4 (light) and 4, grades 5 (light) and 5 (heavy), and 6. The specifications governing fuel oils are similar to those of diesel fuels with some variations. Maximum and minimum specifications for flash point, viscosity, API gravity, ash content, water and sediment contents, distillation end point and amount recovered, sulfur content, cetane number, copper strip corrosion rating, aromaticity, cloud point, and carbon residue are outlined in the standard ASTM D 396 specification for fuel oils.

LUBRICATING OILS

Lubricating oils have very high boiling points (>650°F). Typical carbon ranges are C_{20} to C_{45}+. Normal paraffins (straight chain alkanes) are usually removed by solvent extraction. These materials are enriched in cycloparaffins, aromatics, and nonhydrocarbons and are best characterized on the basis of physical properties such as refractive index, density, and molecular weight. They may contain 70 to 90% alkanes and 10 to 30% aromatics. Greases are lubricating oils to which a thickening agent has been added. Soaps are common additives. See Table II-A-4.

Lubricating oils encompass a wide variety of commercial products used in numerous applications. The carbon number range of a lubricating oil determines the type of application. Refinery processes as well as the type of crude feed determine the type and quality of lubricating oil base stocks that can be used for various applications. Lubricating oils run the gamut of products from automotive and aviation oils, railroad lubricants, marine lubricants, industrial oils including turbine oils, hydraulic oils, cylinder oils, compressor oils, refrigeration oils, and many others too numerous to include here.

The following test specifications may be required for particular lubricating oil formulations: Aniline point, ash and sulfated ash, color, ASTM D 1500, copper strip corrosion, demulsibility, dielectric strength, flash point, fire point, API gravity, interfacial tension, load-carrying ability, neutralization number, oxidation stability, pour point, cloud point, viscosity, and viscosity index. All of these tests help govern the quality of a lubricating oil for a particular application. In some cases, the application dictates the quality of the base stocks utilized, since functionality is a by-product of base stock quality. ASTM D 4485 gives a summary of the specifications for the performance of engine oils. Similar standards for lubricating oils are set by manufacturers of machinery requiring lubricants that conform to particular specifications.

TABLE II-A-4. Lubricant Additive Utilization

	Lubricant Type						
Additive Type	**Engine Oil**	**Transmission Fluids**	**Axle Oils**	**Hydraulic Oils**	**Gear Oils**	**Turbine Oils**	**Metal Working Fluids**
Metallic detergents	•						
Ashless disperants	•	•					
Anti-oxidants	•	•	•	•	•	•	•
Anti-wear agents	•	•	•	•	•		
Rust inhibitors	•			•	•	•	
Corrosion inhibitors	•	•	•				•
Friction modifiers	•	•	•				•
Extreme pressure agents			•		•		•
Anti-foam agents	•	•	•	•	•	•	•
Viscosity improvers	•	•					
Pour point depressants	•	•	•				
Seal swell	•	•					

SUMMARY OF PETROLEUM PRODUCTS COMPOSITION AND SPECIFICATIONS

The composition of gasoline range materials is well characterized. Beyond the gasoline range, the number of isomers is so great that it is not possible to determine individual compounds. In addition, the production of these materials does not require knowledge of detailed compositional information since they are performance-based defined products.

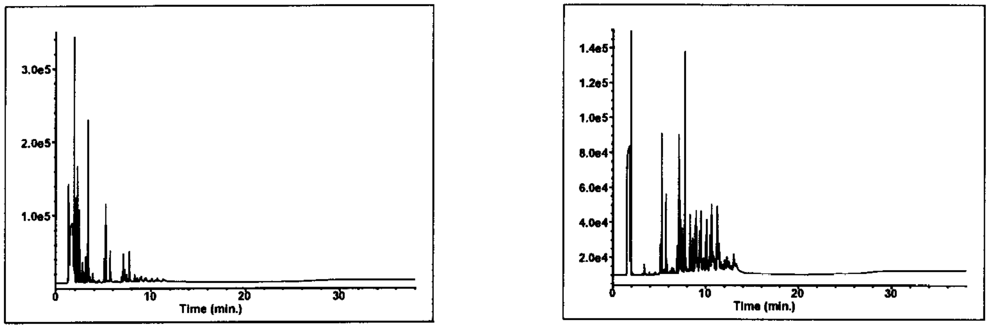
APPENDIX II-B ENVIRONMENTAL FATE OF PETROLEUM PRODUCTS: WEATHERING AND TRANSPORT

Petroleum products released into the environment undergo weathering processes with time. These processes include evaporation, leaching (transfer to the aqueous phase) through solution and entrainment (physical transport along with the aqueous phase), chemical oxidation, and microbial degradation (Christensen and Larsen, 1993). The rate of weathering is highly dependent on environmental conditions. For example, gasoline, a volatile product, will evaporate readily in a surface spill, while gasoline released below 10 feet of clay topped with asphalt will tend to evaporate slowly (weathering processes may not be detectable for years).

Evaporative processes are very important in the weathering of volatile petroleum products, and may be the dominant weathering process for gasoline. Automotive gasoline, aviation gasoline, and JP-4 contain 20% to 99% highly volatile (less than 9 carbon atom) components. Figure II-B-1 shows four gas chromatograms of gasolines that have undergone different amounts of evaporation. The four GC/FID chromatograms in Figure II-B-1 show a dramatic change in composition from the unweathered sample (0% evaporated) to the highly weathered sample (98% evaporated). In each chromatogram, the peaks from 0 to 2 minutes are from a dilution solvent. The most volatile gasoline components elute from (or pass through) the GC between two and seven minutes (visible in the very front of a chromatogram). The GC/FID traces show the loss of these components as the gasoline evaporates.

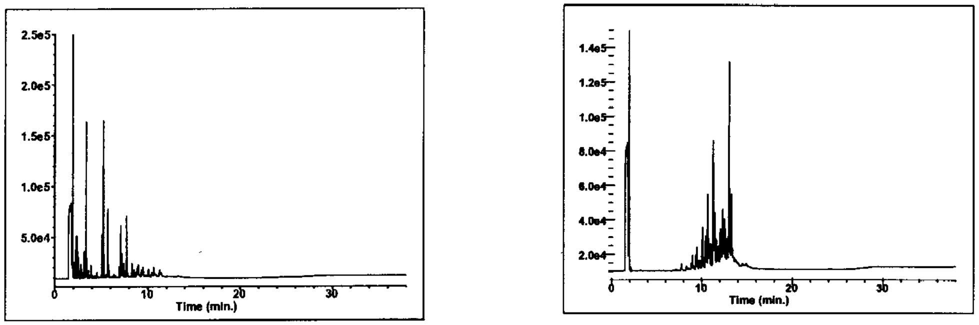
Leaching processes introduce hydrocarbon into the water phase by solubility and entrainment. Aromatics, and especially BTEX, tend to be the most water-soluble fraction of petroleum (Senn and Johnson, 1987). Petroleum contaminated groundwater tends to be enriched in aromatics relative to other petroleum constituents. Relatively insoluble hydrocarbons may be entrained in water through adsorption into kaolinate particles suspended in the water or as an agglomeration of oil droplets (microemulsion) (Coleman et al., 1984). In cases where groundwater contains only dissolved hydrocarbons, it may not be possible to identify the original petroleum product because only a portion of the free product will be present in the dissolved phase. As whole product floats on groundwater, the free product will gradually lose the water-soluble compounds. Whole products have highly distinctive GC fingerprints relative to water-soluble fractions. Groundwater containing entrained product will have a GC fingerprint that is a combination of the free product chromatogram plus enhanced amounts of the soluble aromatics.

Leaching processes of petroleum products in soils can have a variety of potential scenarios. Part of the aromatic fraction of a petroleum spill in soil may partition into water that has been in contact with the contamination. Evaporative processes,



0% Evaporated Gasoline

86% Evaporated Gasoline



58% Evaporated Gasoline

98% Evaporated Gasoline

Figure III-B-1. Evaporative Weathering of Gasolines.

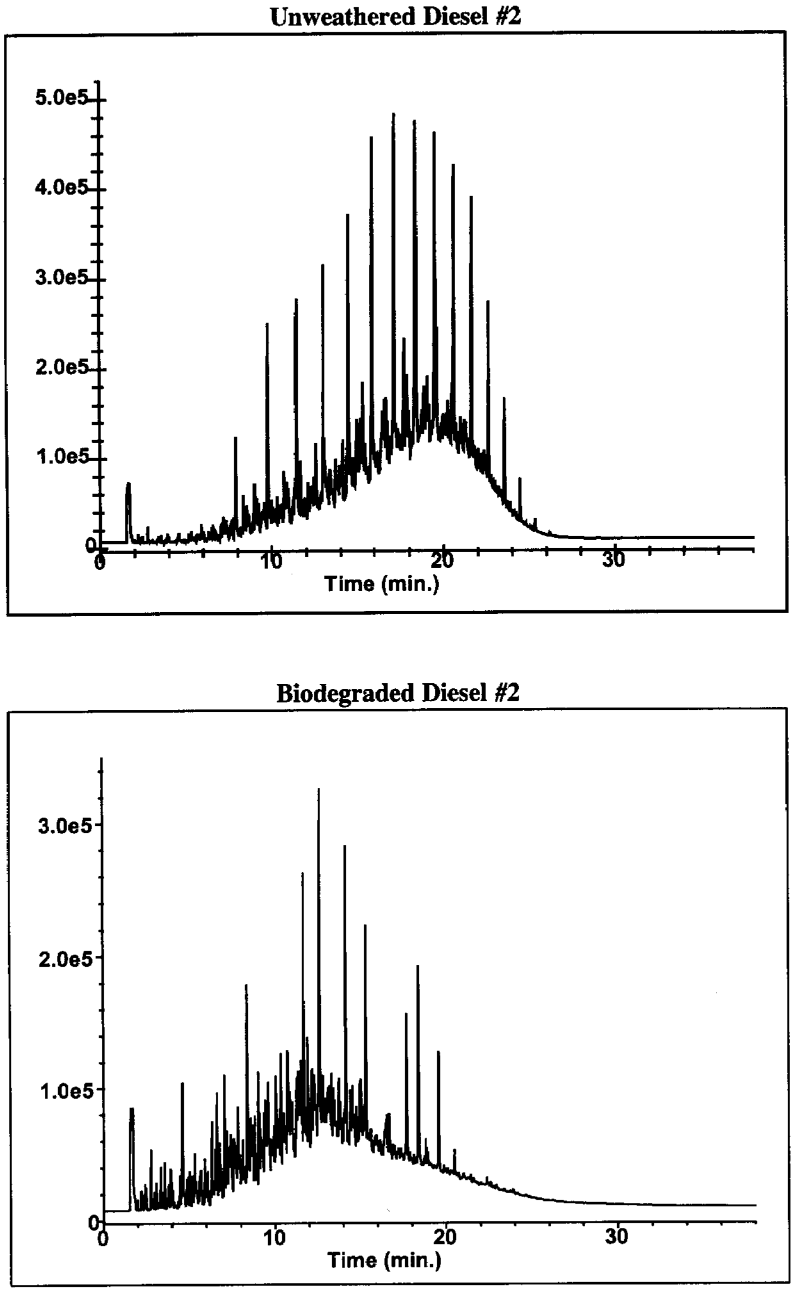


Figure II-B-2. Unweathered Diesel #2.

however, are also working simultaneously to remove the volatile aromatics such as benzene and toluene. A GC characterization of a wet soil sample may sometimes show an unusually high aromatic content.

It is not unusual for a plume of water-soluble aromatics to radiate out from the origin of a spill. Storm drains, pipes, and utility lines may provide conduits for water and water soluble hydrocarbons. Generally, entrained hydrocarbon is found in water close to the petroleum source, while dissolved aromatics may be found quite far from the origin of a spill. Oxygenates, such as methyl-t-butyl ether (MTBE), are even more water soluble than aromatics and are highly mobile in the environment.

Biodegradation processes can be very complex. The extent of biodegradation is dependent on many factors including the type of microorganisms present, environmental conditions (temperature, oxygen levels, moisture etc.), predominant hydrocarbon types, and bioavailability of hydrocarbon contaminants. Evidence indicates that the primary factor controlling the extent of biodegradation is the molecular composition of the soil contaminant. Multiple ring cycloalkanes are hard to degrade, while PAHs display varying degrees of degradation. *n*-Alkanes biodegrade rapidly with branched alkanes and single saturated ring compounds degrading more slowly. Wang et al. (1994) found that samples from a 22-year-old spill of Bunker C oil were >80% depleted in PAHs and that the naphthalenes (diaromatics) were heavily depleted relative to the PAHs.

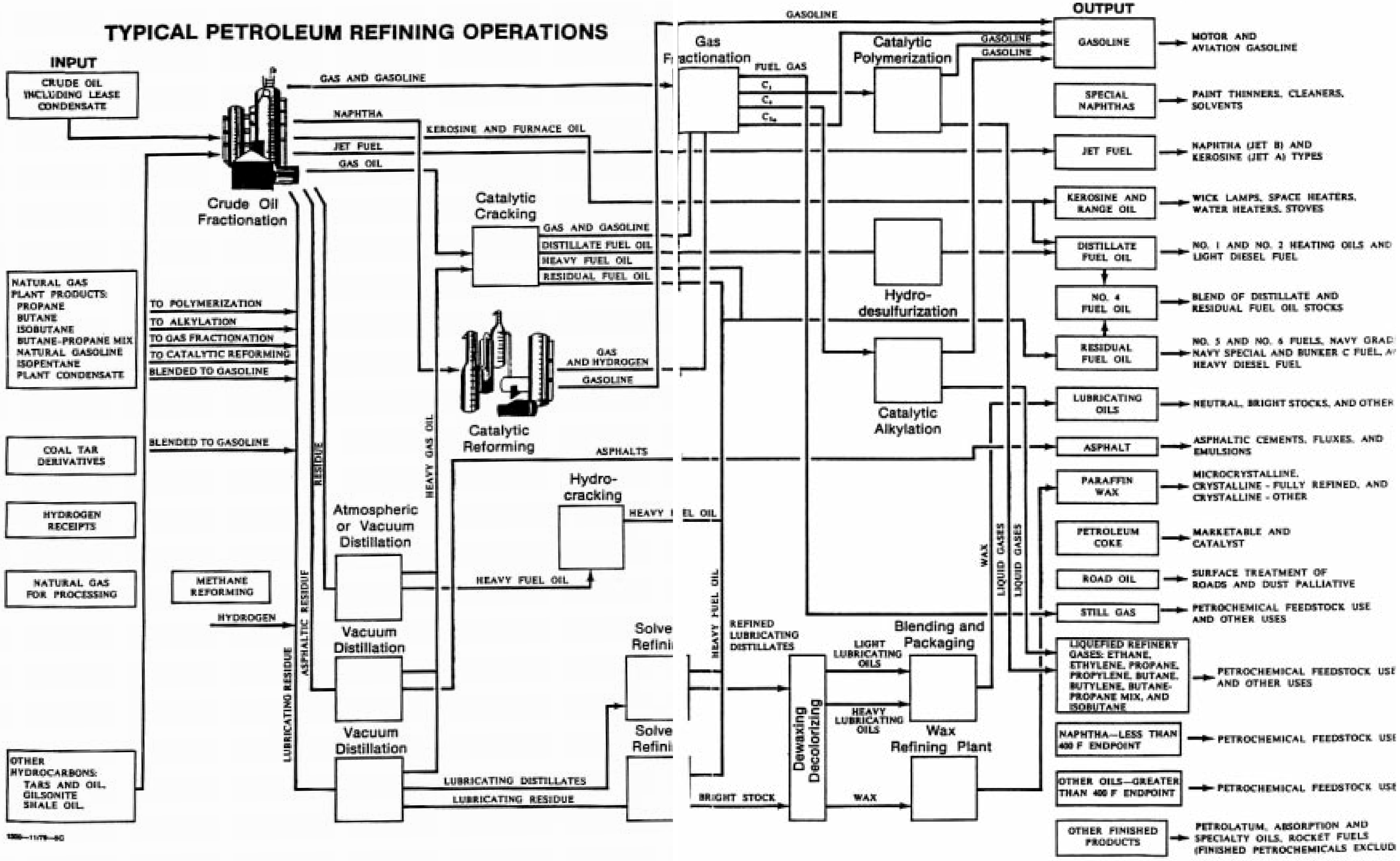
Figure II-B-2 shows one GC/FID chromatogram of fresh diesel #2 and a second GC/FID chromatogram of a weathered diesel #2. The unweathered diesel #2 shows a distinctive pattern of *n*-alkanes. The weathered diesel is depleted of *n*-alkanes, but displays a characteristic pattern of branched alkanes. Signals of two of the branched alkanes, pristane (tetramethyltridecane) and phytane (tetramethyltetradecane), are sometimes compared to signals of their neighboring C_{17} and C_{18} *n*-paraffins, respectively, to evaluate the progress of a bioremediation effort.

An understanding of weathering processes is valuable to environmental test laboratories, bioremediation engineers, and risk assessors. Weathering changes product composition and may affect testing results, the ability to bioremediate, and the toxicity of the spilled product. Unfortunately, the database available on the composition of weathered products is limited.

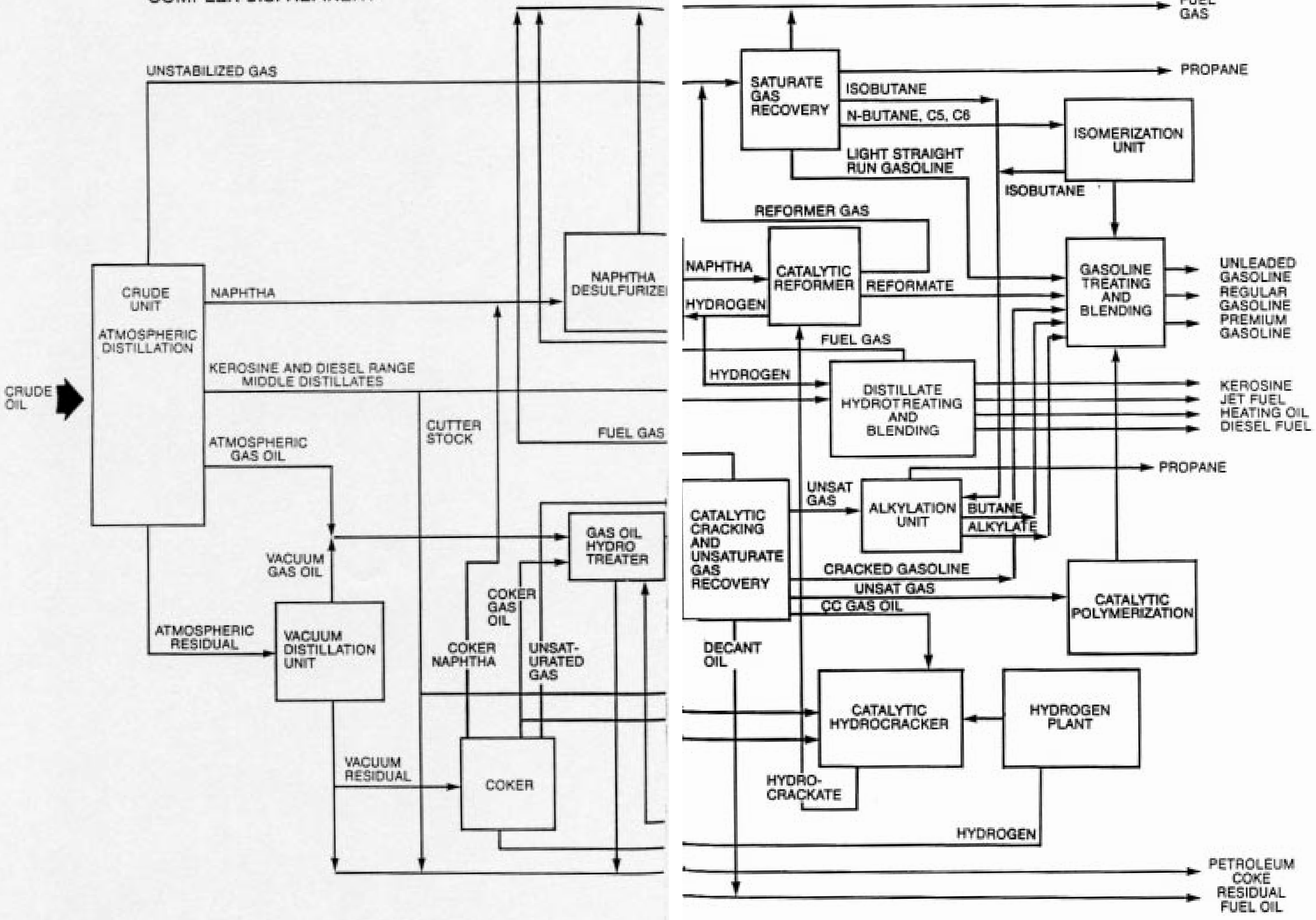
APPENDIX III

Refinery Flow Diagrams

TYPICAL PETROLEUM REFINING OPERATIONS



FLOW DIAGRAM OF A
COMPLEX U.S. REFINERY



APPENDIX IV

Quick Reference of TPH Methods

NON-GC METHODS

				Gravimetric	Immunoassay						Oil & Grease Methods	
NAME	**Modified EPA 418.1**	**TRPH by SFE EXTR'N**	**TPH (Modified ASTM D3921)**	**TPH on Sludge (O&G on Sludge)**	**TPH SCREENING by IMMUNOASSAY**	**BTEX**	**PAHs by GC-MS (subset of 8270)**	**VOC by Purge/trap**	**VOCs in Soil by GC-MS**	**Semi-volatiles by GC-MS**	**O&G (grav., sep funnel)**	**Oil in Soil (CONCAWE)**
GENERAL METHOD TYPE	IR scan of extracted solid sple	Supercritical Fluid Extr'n with IR finish	Mixing extr'n, IR finish	gravimetric, Soxhlet extr'n	Immunoassay Field Test Kit	Capillary purge-trap GC (PID/FID)		Capillary purge-trap GC (PID/EC)	Capillary purge-trap GC-MS		gravimetric., sep funnel	Gravimetric, Erlenmeyer/Soxhlet-type extr'n
METHOD REFERENCE	Method EPA 418.1 but modified.	SW 846 #3560 & 8440 (formerly 9073) (drafts)	Modified from ASTM D3921	SW 846 #9071	SW 846 Method 4030 DRAFT	SW 846 #8020, 602	SW 846 #8250, EPA #625	SW 846 #8021	SW 846 #8240	SW 846 #8270	SW 846 #9070 EPA 413.1	Modified from ASTM D473 ("Sedimentation in fuel oil by extraction")
EXTR'N METHOD REFERENCE		SW 846 #3560 (draft)		same (SW 846 #9071)	SW 846 #3560 (draft)	SW 846 #5030					Same (SW 846 #9070 & EPA 413.1)	Modified ASTM D473
MEASURES	Petroleum Hydrocarbons, oils & fatty matter from animal & vegetables, waxes, organic dyes, sulphur cmpds, chlorophyll & other cmpds.	TPH in diesel range. (gasoline TPH is NOT quantitative). PAHs, PCBs, pesticides, & HCs.	O&G, TPH cmpds which are soluble in CCl4	Non-volatile greases, polar, heavy petroleum hydrocarbons, (not for light hydrocarbons < 70 C)	Cumulatively measures BTEX naphthalene, mineral spirits, creosote, heptane, mixed heptanes, PAHs, aromatics, etc.	Benzene, toluene, ethylbenzene, & xylenes	Polynuclear Aromatic Hydrocarbons (PAHs)	Volatile organics & halogenated volatile organics.			Non-volatile, veg. oils, animal fats, waxes, soaps, greases, etc. (not for light hydrocarbons < 70 C)	O&G, TPH cmpds which are soluble in CCl4
SPLE TYPE	Soils	Soils, sediments, sludge, solids.	soil & solid wastes	sludge	Soil	liquid or solids/soils	Water, soil, sediment, wastes	ground water, aqueous sludges, oily wastes, filter	Soil		liquids	Soil
USE FOR		Diesel & heavier contaminants in soil.	Diesel & heavier contaminants.	Diesel & heavier contaminants.	Gasoline, jet fuel, diesel, fuel oil, & kerosene contamination.			Gasoline & light ends' contamination.			Diesel & heavier contaminants.	Diesel & heavier contaminants.
DO NOT USE FOR		Gasoline in soils.	Gasoline & light ends' contamination cntg volatiles < 70C	Gasoline & light ends' contamination cntg volatiles < 70C	Brake fluid, chain lubricants, greases, lubricating oils, etc.			Diesel & heavier contaminants.			Gasoline & light ends' contamination cntg colatiles < 70C	Gasoline & light ends' contamination cntg volatiles < 70C
INTERFERENCES	Oils & fatty matter from animal & vegetables, waxes, organic dyes, sulphur cmpds, chlorophyll & other cmpds	Animal greases & vegetable oils, if not completely removed by silica gel cleanup procedure.	Oils & fatty matter from animals & vegetables, waxes, organic dyes, sulphur cmpds, chlorophyll & other cmpds.	Oils & fatty matter from animals & vegetables, waxes, organic dyes, sulphur cmpds, chlorophyll & other cmpds.	Sensitivity to all TPH cmpds is NOT equal.	Compounds which may co-elute with BTEX.					Veg. oils, animal fats, waxes, soaps.	Veg. oils, animal fats, waxes, soaps.
PROCEDURE	Freon extr'n, silica gel treatment, IR finish	High temperature/ pressure extr'n into solvent, followed by IR finish.	Acidification, CCl4 extr'n (2 or more times) by stirring for 1 hr each, filtration thru Na2SO4, then IR finish.	Acidification, chemical drying with MgSO4, then Freon extr'n by Soxhlet with gravimetric finish.	Extraction, immunoassay, colorimetric finish.	Extr'n with MeOH then purge-trap GC.					Freon extr'n & gravimetric finish.	CCl4 extr'n & gravimetric finish.
EXTR'N SOLVENT	Freon-113	Tetrachloroethylene	CCl4	Freon-113	MeOH	MeOH					Freon-113	CCl4
EXTR'N PROC	Soxhlet Extr'n	High temperature (80 C)/pressure (340 atm) extr'n into solvent.	Mechanical stirring for 1 hr. Repeated 2 or more times.	Soxhlet for 4 hrs.	1 minute shaking	Shaking (2 min.)					Shaking (2 min.)	Refractory thimble in wide-mouth Erlenmeyer with heated solvent.
PROC. NOTES	Silica gel used to adsorb some polar veg. & animal fats.	Silica gel used to adsorb some polar veg. & animal fats.	Method is entirely empirical and does not relate to other TPH methods because of solvent used.	Method is entirely empirical, and duplicate results can be obtained ONLY by strict adherence to all details of process.		Purge-trap method must be used for groundwater or soil/sediment samples. Do NOT use direct injection.						Modified from extraction method for sediment in crude oils & fuel oils (CCl4 used instead of hot toluene.) Refractory thimble/Erlenmeyer setup is comparable to Soxhlet.
CALIB STD(S)	EPA Reference Oil (3:2:2 n-hexadecane, isooctane, & chlorobenzene)	Same type of petroleum fraction as the contamination. Reference oil to be used for unknowns ONLY.	Same type of petroleum fraction as the contamination. Synthetic std. (isooctane and cetane) to be used for unkowns ONLY.	Check with QC stds	Supplied with the test kit.	Commercial BTEX stds.	Commercial stds.	Commercial stds.	Commercial stds.	Commercial stds.	Check with QC stds.	
ADVANTAGES		1) Extr'n quick (30 min) 2) Minimal solvent 3) NO solvent conc'n steps 4) Doesn't efficiently extract polar humic acids, & chlorophylls.			Screening technique, quick							
DISADVANTAGES	1) Volatile cmpds (i.e., gasoline) lost. 2) High molecular weight hydrocarbons (PNAs, heavy lube oils, residual oils, & asphalt) not extr'd. 3) Not specific for petroleum hydrocarbons. 4) Interferences from veg matter (pine needles, oak leaves, grass etc.) not removed by silica gel treatment.	1) Positive bias if not all interferents removed with silica gel. 2) Higher equipment costs of pressure operations.	1) Only cmpds soluble in CCl4 are measured. 2) Interferences from non-petroleum contaminants. 3) Carbon tetrachloride (CCl4) is known carcinogen.	1) Petroleum fuels (gasoline through #2 fuel oils are completely or partially lost). 2) Freon does not extract heavier TPH cmpds (asphaltenes, some PNAs). 3) Volatiles (< 70C) lost. 4) Freon to be phased out as solvent by end of 1993.	1) NOT accepted for regulatory use, 2) not for light lube oils, greases, brake fluids, chain lubricants, undecane, trichloroetheylene.	Only a limited subset of GRO (and TPH).					1) Petroleum fuels (gasoline through #2 fuel oils) are completely or partially lost. 2) Freon does not extract heavier TPH cmpds (asphaltenes, some PNAs). 3) Volatiles (< 70C) lost. 4) Not for sludges. 5) Liquids only. 6) Freon to be phased out as solvent by end of 1993.	1) Only cmpds soluble in CCl4 are measured. 2) interferences from non-petroleum contaminants. 3) Carbon tetrachloride (CCl4) is a known carcinogen.
NOTES	Use ONLY as screening tool where #2 Fuel Oil or Diesel Fuel in known to be the contamination. Confirm with GC/FID method. Do not use for gasoline contamination.											CONCAWE methods used in the European community. Status similar to ASTM methods.

GC-BASED TPH METHODS

	Gasoline Range Organics methods									"Fingerprint" TPH by GC methods		
NAME	GRO (API)	Cal. LUFT TPH for Gasoline (P/T) in soils	WISCONSIN Modified GRO	ALASKA GRO	Cal. LUFT TPH for Gasoline (Headspace) in soils	DRO (API)	Cal. LUFT TPH for Diesel in soils	WISCONSIN Modified DRO	ALASKA DRO	SHELL (Ileana Rhodes)	TPH by GC (Alaska method)	KWINANA REFINERY (Australia)
GENERAL METHOD TYPE	Capillary purge-trap GC (PID/RD)	Purge/trap witrh GC (RD) analysis	Capillary purge-trap GC (PID/RD)	Capillary purge-trap GC (PID/RD)	Headspace with GC (RD) analysis	Capillary GC (RD)	Extraction then GC (RD) analysis	Capillary GC (RD)	Capillary GC (RD)	Cap. GC (RD) direct inj. of solvent	Cap. GC (RD) direct inj. of solvent	Cap. GC (RD)
METHOD REFERENCE	SW846 #5030, 8000, 8020, 8015, API method eval'n study, EPA TPH Committee.	Dept of Health Services (DHS) method.	SW846 #5030, 8000, 8020, 8015, API method eval'n study, EPA TPH Committee, Wisc. ad hoc Committee on LUST program, & Wisc. State Lab of Hygiene.	SW846 #5030, 8000, 8020, 8015, API method eval'n study, EPA TPH Methods Committee, & Alaska Dept. of Env. Conservation UST Program.	Dept of Health Services (DHS) method.	SW846 #8000, 8100, OA-2, EPA TPH Committee.	Dept of Health Services (DHS) method.	SW846 #8000, 8100, OA-2, EPA TPH Committee, Wisc. ad hoc Committee on LUST program, & Wisc. State Lab of Hygiene	SW846, #8000, 8100, 8015, API consensus method for DRO, EPA TPH Methods Committee, & State of Oregon TPH methods OAR 340-122-350.	Modified 8015	Modified 8015, based on SW846 methods #8000, 8015, 8100, & Ileana Rhodes method. It is similar to Wash. state's WTPH-HCID.	
EXTR'N METHOD REFERENCE	EPA 5030 (purge-trap)	EPA 5030 (purge-trap)	EPA 5030 (purge-trap)	EPA 5030 (purge-trap)	EPA 5020 (headspace)		DHS method					
MEASURES	Gasoline-range organics (C6 - C10 cmpds. with 60 - 170 C bpt.), gasoline, stoddard solvent, mineral spirits.	Gasoline-range organics (C6 - C10 cmpds. with 60 - 220 C bpt.), gasoline, stoddard solvent, mineral	Gasoline-range organics (C6 - C10 cmpds. with 60 - 220 C bpt.), gasoline stoddard solvent, mineral spirits.	Gasoline-range organics (C6 - C10 cmpds. with 60 - 220 C bpt.), gasoline stoddard solvent, mineral spirits.	Volatile gasoline-range components with significant vapor pressure at 90 C.	Diesel, fuel oil #2, kerosine, C10 - C28 cmpds., (not motor oils or lube oils)		Diesel, fuel oil #2, kerosine, C10 - C28 cmpds. (not motor or lube oils)	Diesel, fuel oil #2, kerosine, C10 - C28 cmpds (not motor or lube oils)	GRO TPH + DRO TPH (All GC peaks from solvent to pentacosane.)	GRO TPH DRO TPH (C6 - C25 cmpds with bpt > 70 C)	C6 - C36
SPLE TYPE	Soils	Ground water, sludges, & soils.	Soils	Soils	Soils	Soils/solids	Ground water, sludges, & soils.	Soils	Soils	Soils/solids	Soils/solids	Soils
USE FOR	Gasoline & light ends' contamination in soil.	Gasoline & light ends' contamination in soil.	Gasoline & light ends' contamination in soil.	Gasoline & light ends' contamination in soil.	Gasoline & light ends' contamination in soil.	Diesel	Diesel	Diesel	Diesel or mid-range petroleum products (fuel oils)	Gasoline*, diesel, fuel oil, kerosene contamination. (*See disadvantages below)	Gasoline*, diesel, fuel oil, kerosene contamination. (*See disadvantages below)	Gasoline, diesel, fuel oi, kerosene contamination.
DO NOT USE FOR	Diesel & heavier contaminants in soil.	Diesel & heavier contaminants in soil.	Diesel & heavier contaminants in soil.	Diesel & heavier contaminants in soil.	Diesel & heavier contaminants in soil.	Gasoline, light ends, motor or lube oils.		Gasoline, light ends, motor or lube oils.	Gasoline, light ends, motor or lube oils.	Motor oil, lube oil, heavy product contamination.	Motor oil, lube oil, heavy product contamination.	
INTERFERENCES	Some diesel volatile components, other organic cmpds., chlorinated solvents, ketones, & ethers.	Some diesel volatile components, other organic cmpds., chlorinated solvents, ketones, & ethers.	Some diesel volatile components, other organics cmpds., chlorinated solvents, ketones, & ethers.	Some diesel volatile components, other organic cmpds., chlorinated solvents, ketones, & ethers	Some diesel volatile components, other organic cmpds., solvents ketones, & ethers.	Veg. & animal oils & greases, org. acids, chlorinated hydrocarbons, phenols, phthalate esters, & biogenic terpenes	Veg. & animal oils & greases, org. acids, chlorinated hydrocarbons, phenols, phthalate esters, & biogenic terpenes	Veg. & animal oils & greases, org. acids, chlorinated hydrocarbons, phenols, phthalate esters, & biogenic terpenes	Veg. & animal oils & greases, org. acids, chlorinated hydrocarbons, phenols, phthalate esters, & biogenic terpenes	Industrial solvents, cleaners, & naturally occurring non-petroleum compounds	Industrial solvents, cleaners, vegetable & animal oils & greases, organic acids, cholorinated hydrocarbons, phenols, phthalate esters & naturally occurring non-petroleum compounds	Veg. & animal oils & grease, org. acids, chlorinated hydrocarbons, phenols, phthalate esters, & biogenic terpenes
PROCEDURE	MeOH extr'n by shaking (2 min.), then purge-trap GC analysis.	MeOH extr'n by shaking (2 min.) then purge-trap GC analysis. External calibration curves used.	MeOH extr'n by shaking (2 min) then sonication (20 min), & purge-trap GC analysis.	Immersion in MeOH at time of spl'g., extr'n by shaking (2 min), & purge-trap GC analysis of extract.	Headspace analysis from 90 C sple (External std technique). External calibration curves used.	3 X Solvent extr'n with Na2SO4 added (to dry), sonication with horn-type sonicator (1.5 min), Kuderna-Danish extract concentration, GC analysis	Mechanical shaking (4 hrs), Na2SO4 drying, Kuderna-Danish conc'n, then direct injection into GC. Analysis by external std technique.	2 X Solvent extr'n (20 min) with Na2SO4 added (to dry), sonication in water bath, extract concentration, silica gel cleanup (opt'l), GC analysis.	Chemical drying with Na2SO4, MeCl2 extraction using sonication (3 X) or Soxhlet extraction (18-24 hrs), extract concentration, GC analysis.	Cap. GC (RD) direct inj of solvent after extr'n.	Chemically dry with Na2SO4, solvent extr'n by shaking or sonication, then direct injection onto capll'y GC (RD).	
EXTR'N SOLVENT	MeOH	CS2 (Alternative solvents = ethyl acetate or MeCl2)	MeOH	MeOH (in field)	None	MeCl2	CS2 (Alternative solvents = ethyl acetate or MeCl2)	Hexane*, MeCl2, or CS2. *recommended.	MeCl2	GRO Only - MeOH DRO - MeCl2 GRO/DRO mxts-MeCl2	MeCl2	MeCl2
EXTR'N PROC	Shaking (2 min.)	Shaking.	Ultrasonic bath.	Shaking.	None	Sonication using ultrasonic cell disrupter (horn-type).	Mechanical shaking (4 hrs), Na2SO4 drying, then Kuderna-Danish conc'n	Ultrasonic bath.	Horn-type sonicator or Soxhlet extr'n	1-4 hrs shaking	1 min vortex mixing + 1-4 hrs shaking, OR 2 X ultrasonic bath (5 min. each time)	Ultrasonic bath (30 min)
PROC. NOTES		External Std technique used to quantify results.			External Std technique used to quantify results.	Silica gel used to adsorb some polar veg. & animal fats. (opt'l)	External Std technique used to quantify results.	Silica gel used to adsorb some polar veg. & animal fats. (opt'l)	Dry sple with Mg2SO4 before Extr'n.	If > 10% moisture, dry sple with Na2SO4 before Extr'n.	If > 10% moisture, dry sple with Na2SO4 before Extr'n	Na2SO4 or MgSO4 to dry all sples.
CALIB STD(S)	Gasoline component standard in MeOH (2-methylpentane, 2, 2, 4-trimethylpentane, heptane, benzene toluene, ethylbenzene, m-, p-, o-xylene, 1, 2, 4-trimethylbenzene) OR actual GASOLINE as std.	Commercial Gasoline std in dodecane,	Gasoline component standard in MeOH (3-methylpentane, isooctane, benzene, toluene, ethylbenzene m-, p-, o-xylene, 1, 2, 4-trimethylbenzene naphthalene)	1:1:1 mxt of unleaded, leaded, and premium commercial gasoline In MeOH	Commercial Gasoline std in dodecane,	Diesel component std. (decane, dodecane, tetradecane, hexadecane, octadecane, eicosane, decosane, tetracosane, hexacosane, octacosane.) OR actual FUEL (kerosine, diesel) as std.	Commercial Diesel std in CS2 (or other solvent)	Diesel component std. (decane, dodecane, tetradecane, hexadecane, octadecane, eicosane, decosane, tetracosane, hexacosane, octacosane.)	1:1:1 mxt artic diesel, diesel 1, and diesel 2 (If arctic diesel unavailable, kerosene may be substituted)	GRO - Gasoline DRO - Diesel Mxt. - Gasoline/diesel Synthetic Mxt	GRO - Gasoline DRO - Diesel Mxt. - Gasoline/diesel Synthetic Mxt	Diesel
ADVANTAGES		External std calibration technique corrects for loss of volatiles in procedure.		Less bias due to use of commercial gasoline std. External std calibration corrects for loss of volatiles in procedure.	External std calibration technique corrects for loss of volatiles in procedure.		External std calibration technique corrects for loss of volatiles in procedure.					
DISADVANTAGES	1) Negative bias (55-75% for gasoline in Ottawa sand) due to presence of volatiles <C6 (i.e. there 10% ethanol in gasoline which is not measured.) Another calib std. would reduce this bias.		1) Negative bias (55-75% for gasoline in Ottawa sand) due to presence of volatiles <C6 (i.e. there 10% ethanol in gasoline which is not measured.) Another calib std. would reduce this bias.		1) Only remaining volatiles measured. 2) Poor for weathered samples.					1) Spies cntg < C6 cmpds obscured by solvent peak & therefore biased low unless gasoline std used for gasoline-contaminated sples. Use of synthetic stds underestimate TPH.	1) Spies cntg < C6 cmpds obscured by solvent peak & therefore biased low unless gasoline std used for GRO sples. 2) Use of synthetic stds underestimate TPH.	
NOTES	Measures all peaks btw 2-methylpentane & 1, 2, 4-trimethylbenzene.		Measures all peaks btw 3-methylpentane & naphthalene.	Measures all peaks between & including C6 (2-methyl pentane) & C9 (1, 2, 4-trimethylbenzene).				*The modified GRO & DRO methods are equivalent to & replace the "TPH as gasoline" & "TPH as diesel" analyses. (4-1-92)*				
	Prescreening recommended by direct GC analysis, headspace analysis (3810), or hexadecane extr'n & screening (3820).		Prescreening recommended by direct GC analysis, headspace analysis (3810), or hexadecane extr'n & screening (3820).	Prescreening recommended by Direct GC anaysis, headspace analysis (3810), or hexadecane extr'n & screening (3820).								
			The modified GRO & DRO methods are equivalent to & replace the "TPH as gasoline" & "TPH as diesel" analyses. (4-1-92)									

EXPLANATION OF ACRONYMS

AAR	American Association of Railroads
AEHS	Association for the Environmental Health of Soils
API	American Petroleum Institute
ASME	American Society of Mechanical Engineers
ASTM	American Society for Testing and Materials
BP	British Petroleum
BTEX	Benzene, Toluene, Ethylbenzene, and Xylenes
DOD	Department of Defense
DOE	Department of Energy
DOT	Department of Transportation
DRO	Diesel Range Organics
EDB	Ethylene Dibromide
EDC	Ethylene Dichloride
EPH	Extractable Petroleum Hydrocarbons
FID	Flame Ionization Detector
GC	Gas Chromatography
GC/MS	Gas Chromatography/Mass Spectrometry
GRI	Gas Research Institute
GRO	Gasoline Range Organics
HPLC	High Performance Liquid Chromatography
IR	Infrared
LC	Liquid Chromatography
MMT	Methylcyclopentadienyl Manganese Tricarbonyl
MON	Motor Octane Number
MTBE	Methyl Tertiary-butyl Ether
NACE	National Association of Corrosion Engineers
NPDES	National Pollutant Discharge Elimination System
O&G	Oil and Grease
PAH	Polycyclic Aromatic Hydrocarbon
PHC	Petroleum Hydrocarbon
PIANO	Paraffins, Isoparaffins, Naphthenes, Olefins, and Aromatics
PID	Photoionization Detector

PNA	Polynuclear Aromatic
PPM	Part Per Million
RBCA	Risk-Based Corrective Action
RON	Research Octane Number
SFE	Supercritical Fluid Extraction
SPE	Solid Phase Extraction
SPME	Solid Phase Micro-extraction
SVOC	Semi-volatile Organic Compound
TBA	Tert-butyl Alcohol
TEL	Tetraethyl Lead
TLC	Thin Layer Chromatography
TPH	Total Petroleum Hydrocarbons
TPHCWG	Total Petroleum Hydrocarbon Criteria Working Group
TPH-D	Total Petroleum Hydrocarbons-Diesel
TPH-G	Total Petroleum Hydrocarbons-Gasoline
TPHV	Total Petroleum Hydrocarbons Volatiles
TRPH	Total Recoverable Petroleum Hydrocarbons
UCM	Unresolved Complex Mixture
USEPA	United States Environmental Protection Agency
UV	Ultraviolet
VM&P	Varnish Maker’s and Painter’s [naptha], i.e. paint thinner
VOC	Volatile Organic Compound
VPH	Volatile Petroleum Hydrocarbons

GLOSSARY OF TERMS

Additive	A substance added to petroleum mixtures (e.g., lubricating oils) to impart new or to improve existing characteristics.
Aliphatic hydrocarbon	Hydrocarbons in which the carbon-hydrogen groupings are arranged in open chains which may be branched. The term includes *paraffins* and *olefins* and provides a distinction from *aromatics* and *naphthenes,* which have at least some of their carbon atoms arranged in closed chains or rings.
Alkanes	Hydrocarbons that contain only single bonds. The chemical name indicates the number of carbon atoms and ends with the suffix "–ane".
Alkenes	Hydrocarbons that contain carbon-carbon double bonds. The chemical name indicates the number of carbon atoms and ends with the suffix "ene".
Alkyl groups	A group of carbon and hydrogen atoms that branch from the main carbon chain or ring in a hydrocarbon molecule. The simplest alkyl group, a methyl group, is a carbon atom attached to three hydrogen atoms.
Analyte	The chemical for which a sample is tested, or analyzed.
Antibody	A molecule having chemically reactive sites specific for certain other molecules.
Aromatic	A compound containing one or more conjugated rings that also may contain sulfur, nitrogen, and oxygen.
Asphaltene	A constituent of petroleum products with a high molecular mass and dark color, insoluble in *n*-heptane, and soluble in hot benzene.
ASTM	American Society for Testing and Materials, responsible for many of the standard methods used in the petroleum industry.
Biogenic	Bacterial or vegetation derived material.
Biological lipids	Any biological fluids that are miscible with a nonpolar solvent. These materials include waxes, essential oils, chlorophyll, etc.
Boiling point	A characteristic physical property of a liquid at which the vapor pressure is equal to that of the atmosphere and the liquid is converted to a gas.

BTEX	Benzene, toluene, ethylbenzene, and the xylene isomers.
Bunker fuel	Heavy *residual oil*, also called bunker C, bunker C fuel oil, or bunker oil.
Chromatogram	The resultant electrical output of sample components passing through a detection system following chromatographic separation. A chromatogram may also be called a *trace*.
Cleanup	A preparatory step following extraction of a sample media designed to remove components that may interfere with subsequent analytical measurements.
Confirmation column	A secondary column in chromatography that contains a stationary phase having different affinities for components in a mixture than in the primary column. Used to confirm analyses that may not be completely resolved using the primary column.
Cracking	A process whereby the relative proportion of lighter or more volatile components of an oil is increased by changing the chemical structure of the constituent hydrocarbons.
Crude oil	Naturally occurring mixture consisting essentially of many types of hydrocarbons, but also containing sulfur, nitrogen or oxygen derivatives. Crude oil may be of paraffinic, asphaltic or mixed base, depending on the presence of *paraffin* wax and *bitumen* in the *residue* after atmospheric distillation. Crude oil composition varies according to the geological strata of its origin.
Cut	The *distillate* obtained between two given temperatures during a distillation process.
Cycloalkane	A class of alkanes that are in the form of a ring.
Cycloparaffin	An example of a cycloalkane.
Diesel fuel	That portion of *crude oil* that distills out within the temperature range approximately 200-370°C. A general term covering oils used as fuel in diesel and other compression ignition engines.
Distillate	A product obtained by condensing the vapors evolved when a liquid is boiled and collecting the condensation in a receiver that is separate from the boiling vessel.
Distillation range	A single pure substance has one definite boiling point at a given pressure. A mixture of substances, however, exhibits a range of temperatures over which boiling or distillation commences, proceeds and finishes. This range of temperatures, determined by means of standard apparatus, is termed the ‘distillation’ or ‘boiling’ range.

Eluate	The solutes, or analytes, moved through a chromatographic column (see *elution*).
Eluent	Solvent used to elute sample.
Elution	Process whereby a solute is moved through a chromatographic column by a solvent (liquid or gas), or eluent.
Extract	In solvent extraction, the portion of a sample preferentially dissolved by the solvent and recovered by physically separating the solvent.
"Fingerprint" analysis	A direct injection GC/FID analysis in which the detector output - the chromatogram - is compared to chromatograms of reference materials as an aid to product identification.
Flame ionization detector (FID)	A detector for a gas chromatograph that measures any thing that can burn.
Fuel oil	A general term applied to oil used for the production of power or heat. In a more restricted sense, it is applied to any petroleum product that is used as boiler fuel or in industrial furnaces. These oils are normally *residues*, but blends of distillates and *residues* are also used as fuel oil. The wider term, '*liquid fuel*,' is sometimes used, but the term 'fuel oil' is preferred.
Gas chromatography	An analytical technique, employing a gaseous mobile phase, that separates mixtures into their individual components.
Gas oil	A petroleum distillate with a viscosity and *distillation range* intermediate between those of *kerosene* and *light lubricating oil*.
Gasoline (petrol)	Refined petroleum distillate, normally boiling within the limits of 30-220°C, which, combined with certain additives, is used as fuel for spark-ignition engines. By extension, the term is also applied to other products that boil within this range.
Gravimetric	Gravimetric methods weigh a residue.
Grease	A semisolid or solid lubricant consisting of a stabilized mixture of mineral, fatty, or synthetic oil with soaps, metal salts, or other thickeners.
Headspace	The vapor space above a sample into which volatile molecules evaporate. Certain methods sample this vapor.
Heating oil	*Gas oil* or *fuel oil* used for firing the boilers of central heating systems.

Hydraulic fluid	A fluid supplied for use in hydraulic systems. Low viscosity and low *pour-point* are desirable characteristics. Hydraulic fluids may be of petroleum or nonpetroleum origin.
Hydrocarbons	Molecules that consist only of hydrogen and carbon atoms.
Immunoassay	Portable tests that take advantage of an interaction between an antibody and a specific analyte. Immunoassay tests are semi-quantitative and usually rely on color changes of varying intensities to indicate relative concentrations.
Infrared spectroscopy	An analytical technique that quantifies the vibration (stretching and bending) that occurs when a molecule absorbs (heat) energy in the infrared region of the electromagnetic spectrum.
Jet fuel	*Kerosene* or *gasoline/kerosene* mixture for fueling aircraft *gas turbine* engines.
Kerosene	A refined petroleum *distillate* intermediate in volatility between gasoline and gas oil. Its *distillation* range generally falls within the limits of 150 and 300°C. Its main uses are as a jet engine fuel, an illuminant, for heating purposes, and as a fuel for certain types of internal combustion engines.
Light distillate	A term lacking precise meaning, but commonly applied to *distillates*, the *final boiling-point* of which does not exceed 300°C.
Liquid chromatography	A chromatographic technique which employs a liquid mobile phase.
Liquid/liquid extraction	An extraction technique in which one liquid is shaken with or contacted by an extraction solvent to transfer molecules of interest into the solvent phase.
Mass spectrometer	An analytical technique that "fractures" organic compounds into characteristic "fragments" based on functional groups that have a specific mass-to-charge ratio.
Middle distillate	One of the distillates obtained between *kerosene* and *lubricating oil* fractions in the refining processes. These include *light fuel oils* and *diesel fuels*.
Mineral hydrocarbons	Petroleum hydrocarbons, considered "mineral" because they come from the earth rather than from plants or animals.
Mobile phase	In chromatography, the phase (gaseous or liquid) responsible for moving an introduced sample through a porous medium to separate components of interest.

Naphtha	*Straight-run* gasoline fractions boiling below *kerosene* and frequently used as a *feedstock* for *reforming* processes. Also known as *heavy benzine* or *heavy gasoline*.
Naphthene	Petroleum industry term for a *cycloparaffin (cycloalkane)*.
Olefin	Synonymous with *alkene*.
Oxygenated gasolines	Gasolines with added ethers or alcohols, formulated according to the Federal Clean Air Act to reduce carbon monoxide emissions during winter months.
Polycyclic aromatic hydrocarbons (PAHs)	PAHs consist of a suite of compounds comprised of two or more aromatic rings. PAHs are found in many petroleum mixtures, and they are predominantly introduced to the environment through natural and anthropogenic combustion processes.
Paraffin (alkanes)	One of a series of saturated aliphatic hydrocarbons, the lowest numbers of which are methane, ethane, and propane. The higher homologues are solid waxes.
Partitioning	In chromatography, the physical act of a solute having different affinities for the stationary and mobile phases. Partition ratios, K, are defined as the ratio of total analytical concentration of a solute in the stationary phase, C_S, to its concentration in the mobile phase, C_M.
Photoionization detector (PID)	A gas chromatographic detection system which utilizes an ultraviolet lamp as an ionization source for analyte detection. It is usually used as a selective detector by changing the photon energy of the ionization source.
Positive bias	A result that is incorrect and too high.
Purge and trap	A chromatographic sample introduction technique in volatile components which are “purged” from a liquid medium by bubbling gas through it. The components are then concentrated by “trapping” them on a short intermediate column, which is subsequently heated to drive the components on to the analytical column for separation.
Purge gas	Typically helium or nitrogen, used to remove analytes from the sample matrix in purge/trap extractions.
Retention time	The time it takes for an eluate to move through a chromatographic system and reach the detector. Retention times are reproducible and can therefore be compared to a standard for analyte identification.
Separatory funnel	Glassware shaped like a funnel with a stoppered rounded top and a valve at the tapered bottom, used for liquid/liquid separations.

Soap	An emulsifying agent made from sodium or potassium salts of fatty acids.
Solvent	Fluids in which certain kinds of molecules dissolve. While they typically are liquids with low boiling points, they may include high-boiling liquids, supercritical fluids, or gases.
Sonication	A physical technique employing ultrasound to intensely vibrate a sample media in extracting solvent and to maximize solvent / analyte interactions.
Soxhlet extraction	An extraction technique for solids in which the sample is repeatedly contacted with solvent over several hours, increasing extraction efficiency.
Stationary phase	In chromatography, the porous solid or liquid phase through which an introduced sample passes. The different affinities the stationary phase has for a sample allow the components in the sample to be separated, or resolved.
Supercritical fluid extraction	An extraction method where the extraction fluid, usually CO_2, is present at a pressure and temperature above its critical point.
Target analyte	Target analytes are compounds that are required analytes in U.S. EPA analytical methods. BTEX and PAHs are examples of petroleum-related compounds that are target analytes in U.S. EPA Methods.
Thin layer chromatographiy (TLC)	A chromatographic technique employing a porous medium of glass coated with a stationary phase. An extract is spotted near the bottom of the medium and placed in a chamber with solvent (mobile phase). The solvent moves up the medium and separates the components of the extract, based on affinities for the medium and solvent.
TPH E	Gas chromatographic test for TPH extractable organic compounds.
TPH V	Gas chromatographic test for TPH volatile organic compounds.
TPH-D(DRO)	Gas chromatographic test for TPH diesel-range organics.
TPH-G(GRO)	Gas chromatographic test for TPH gasoline-range organics.
Unresolved complex mixture (UCM)	The thousands of compounds that a gas chromatograph is unable to fully separate.

Volatile compounds	“Volatile” is relative. It may mean (1) any compound which will purge, (2) any compound which will elute before the solvent peak (usually those $< C_6$), or (3) any compound which will not evaporate during a solvent removal step.
Wax	Waxes of petroleum origin consist primarily of normal paraffins. Waxes of plant origin consist of esters of unsaturated fatty acids.

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