3. IDENTITY AND ANALYSIS OF TOTAL PETROLEUM HYDROCARBONS

3.1 INTRODUCTION

Petroleum hydrocarbons (PHCs) are common site contaminants, but they are not generally regulated as hazardous wastes. Methods for sampling and analysis of environmental media for the family of PHCs are generally thought of as TPH methods. For purposes of this profile, the term TPH refers not only to analytical results, but also to environmental and health properties of PHCs. In part due to the complexity of TPH components themselves, little is known about their potential for health or environmental impacts. As gross measures of petroleum contamination, TPH results simply show that petroleum hydrocarbons are present in the sampled media. Measured TPH values suggest the relative potential for human exposure and, therefore, the relative potential for human health effects. The assessment of health effects due to TPH exposure requires much more detailed information than what is provided by a single TPH value. This chapter, Chapter 5, and the accompanying Appendix E provide more detailed physical and chemical properties and analytical information on TPH and its components.

The federal government has left much of the specific regulation and oversight of crude oil production/ refining to the states. Leaking underground storage tanks (LUST) are the most frequent causes of federal and state governmental involvement in petroleum hydrocarbon problems. Soil contamination has been a growing concern, because it can be a source of groundwater (drinking water) contamination; contaminated soils can reduce the usability of land for development; and weathered petroleum residuals may stay bound to soils for years. Positive TPH test results may require action on the part of land owners, local or state governments, and engineering firms called on to remove or reduce the TPH problem.

ATSDR has the responsibility for health assessment at National Priorities List (NPL) hazardous waste sites, many of which have petroleum hydrocarbon contamination. Specific contaminants that are components of TPH, such as BTEX (benzene, toluene, ethylbenzene, and xylene), *n*-hexane, jet fuels, fuel oils, and mineral-based crankcase oil, have been studied by ATSDR and a number of toxicological profiles have been developed on individual constituents and petroleum products. The

ATSDR profiles relevant to petroleum products are listed in Table 3- 1. However, TPH itself has not been as extensively studied by ATSDR and no previous profile was developed. Although several toxicological profiles have been developed for petroleum products and for specific chemicals found in petroleum, TPH test results have been too nonspecific to be of real value in the assessment of its potential health effects.

Several approaches are discussed in this document for interpreting TPH and related analytical results. The TPH approach taken by EPA and others, through the mid-1990s, followed general risk assessment approaches for chemical mixtures. In all approaches there is a need to reduce a comprehensive list of potential petroleum hydrocarbons to a manageable size. Depending on how conservative the approach is, methods that have been used select: (1) the most toxic among the TPH compounds (indicator approach); (2) one or more representative compounds (surrogate approach, but independent of relative mix of compounds); or (3) representative compounds for fractions of similar petroleum hydrocarbons. ATSDR has taken, in part, the third approach in keeping with the Total Petroleum Hydrocarbons Criteria Working Group (TPHCWG), but has developed its own set of TPH fraction representatives, many of which overlap those of the TPHCWG. In addition, this profile provides information on petroleum products, where such information exists. TPH risk (screening) values for fractions presented in this profile are based on the ATSDR MRLs previously developed for individual constituents and petroleum products. These MRLs are summarized in Appendix A. This fraction approach is the most demanding in information gathering and because of that would appear to be the most rigorous approach to date. Sections 6.1.2 and 6.1.3 contain a more comprehensive discussion of the approaches. The identity, chemical-physical, and analytical information discussed and listed in this chapter, in Appendices D and E, and in Chapter 5 are integral to defining TPH.

3.2 CHEMICAL AND PHYSICAL INFORMATION

Petroleum products are complex mixtures of hundreds of hydrocarbon compounds, ranging from light, volatile, short-chained organic compounds to heavy, long-chained, branched compounds. The exact composition of petroleum products varies depending upon (1) the source of the crude oil (crude oil is derived from underground reservoirs which vary greatly in their chemical composition) and (2) the refining practices used to produce the product.

Table 3-1. ATSDR Profiles with Information on Analytical Methods Relevant to Petroleum Products

Petroleum product	Reference
Jet Fuels, JP-4/JP-7	ATSDR 1995c
Jet Fuels, JP-5/JP-8	ATSDR 1998b
Stoddard solvent	ATSDR 1995b
Automotive gasoline	ATSDR 1995a
Fuel oils	ATSDR 1995g
Crankcase oil	ATSDR 1997c
Benzene	ATSDR 1997a
Toluene	ATSDR 1994
Ethylbenzene	ATSDR 1999a
Xylenes	ATSDR 1995d
Naphthalene	ATSDR 1995e
Methyl *t*-butyl ether	ATSDR 1996a
Polycyclic aromatic hydrocarbons	ATSDR 1995f
Hexane	ATSDR 1999b
Mineral oil (hydraulic fluids)	ATSDR 1997b

During the refining process, crude oil is separated into fractions having similar boiling points. These fractions are then modified by cracking, condensation, polymerization, and alkylation processes, and are formulated into commercial products such as naphtha, gasoline, jet fuel, and fuel oils. The composition of any one of these products can vary based on the refinery involved, time of year, variation in additives or modifiers, and other factors. The chemical composition of the product can be further affected by weathering and/or biological modification upon release to the environment. The following subsections present overviews of petroleum products. Also, a master list of individual aliphatic and aromatic compounds found in TPH is provided in Appendix D. Further information on whole petroleum products, their identity, major components, and physical/chemical properties is found in Appendix E.

Automotive Gasoline. Automotive gasoline is a mixture of low-boiling hydrocarbon compounds suitable for use in spark-ignited internal combustion engines and having an octane rating of at least 60. Additives that have been used in gasoline include alkyl tertiary butyl ethers (e.g. MTBE), ethanol (ethyl alcohol), methanol (methyl alcohol), tetramethyl-lead, tetraethyl-lead, ethylene dichloride, and ethylene dibromide.

Other categories of compounds that may be added to gasoline include anti-knock agents, antioxidants, metal deactivators, lead scavengers, anti-rust agents, anti-icing agents, upper-cylinder lubricants, detergents, and dyes (ATSDR 1995a).

Automotive gasoline typically contains about 150 hydrocarbon compounds, though nearly 1,000 have been identified (ATSDR 1995a). The relative concentrations of the compounds vary considerably depending on the source of crude oil, refinery process, and product specifications. Typical hydrocarbon chain lengths range from C_4 through C_{12} with a general hydrocarbon distribution consisting of 4-8% alkanes, 2-5% alkenes, 25-40% isoalkanes, 3-7% cycloalkanes, l-4% cycloalkenes, and 20-50% aromatics (IARC 1989a). However, these proportions vary greatly. Unleaded gasolines may have higher proportions of aromatic hydrocarbons than leaded gasolines.

Table E-1.b (Appendix E) presents ranges and weight percentage means for a representative subset of the hydrocarbon compounds identified in gasoline. In cases where data are not available, the range and mean are left blank.

Stoddard Solvent. Stoddard solvent is a petroleum distillate widely used as a dry cleaning solvent and as a general cleaner and degreaser. It may also be used as a paint thinner, as a solvent in some types of photocopier toners, in some types of printing inks, and in some adhesives. Stoddard solvent is considered to be a form of mineral spirits, white spirits, and naphtha; however, not all forms of mineral spirits, white spirits, and naphtha are considered to be Stoddard solvent (ATSDR 1995b).

Stoddard solvent consists of 30-50% linear and branched alkanes, 30-40% cycloalkanes, and lo-20% aromatic hydrocarbons. Its typical hydrocarbon chain ranges from C_7 through C_{12} in length.

Although a complete list of the individual compounds comprising Stoddard solvent is not available (Air Force 1989) some of the major components are presented in Table E-2.b (Appendix E). Alcohols, glycols, and ketones are not included in the composition, as few, if any, of these types of compounds would be expected to be present in Stoddard solvent (ATSDR 1995b). Possible contaminants may include lead (<1 ppm) and sulfur (3.5 ppm).

Jet Fuel. Jet fuels are light petroleum distillates that are available in several forms suitable for use in various types ofjet engines. The exact compositions of jet fuels are established by the U.S. Air Force, using specifications that yield maximum performance by the aircraft. The major jet fuels used by the military are JP-4, JP-5, JP-6, JP-7, and JP-8. Briefly, JP-4 is a wide-cut fuel developed for broad availability in times of need. JP-6 is a higher cut than JP-4 and is characterized by fewer impurities. JP-5 is specially blended kerosene, and JP-7 is a high flash point special kerosene used in advanced supersonic aircraft. JP-8 is a kerosene modeled on Jet A-l fuel (used in civilian aircraft). For this profile, JP-4 will be used as the prototype jet fuel due to its broad availability and extensive use.

Typical hydrocarbon chain lengths characterizing JP-4 range from C_4 to C_{16}. Aviation fuels consist primarily of straight and branched alkanes and cycloalkanes. Aromatic hydrocarbons are limited to 20-25% of the total mixture because they produce smoke when burned. A maximum of5% alkenes are allowed in JP-4 (ATSDR 1995c). The approximate distribution by chemical class is: 32% straight alkanes, 31% branched alkanes, 16% cycloalkanes, and 21% aromatic hydrocarbons (ABB Environmental 1990). The typical hydrocarbon composition of JP-4 is presented in Table E-3.b (Appendix E).

Fuel Oil #1. Fuel oil #l is a petroleum distillate that is one of the most widely used of the fuel oil types. It is used in atomizing burners that spray fuel into a combustion chamber where the tiny droplets bum while in suspension. It is also used as a carrier for pesticides, as a weed killer, as a mold release agent in the ceramic and pottery industry, and in the cleaning industry. It is found in asphalt coatings, enamels, paints, thinners, and varnishes.

Fuel oil #1 is a light petroleum distillate (straight-run kerosene) consisting primarily of hydrocarbons in the range C_9-C_{16} (ATSDR 19958). Fuel oil #l is very similar in composition to diesel fuel oil #l; the primary difference is in the additives. The typical hydrocarbon composition of fuel oil #l is presented in Table E-4.b (Appendix E).

Fuel Oil #2. Fuel oil #2 is a petroleum distillate that may be referred to as domestic or industrial. The domestic fuel oil #2 is usually lighter and straight-run refined; it is used primarily for home heating and to produce diesel fuel #2. Industrial distillate is the cracked type, or a blend of both. It is used in smelting furnaces, ceramic kilns, and packaged boilers (ABB Environmental 1990).

Fuel oil #2 is characterized by hydrocarbon chain lengths in the C_{11}-C_{20} range, whereas diesel fuels predominantly contain a mixture of C_{10}-C_{19} hydrocarbons (ATSDR 1995g). The composition consists of approximately 64% aliphatic hydrocarbons (straight chain alkanes and cycloalkanes), l-2% unsaturated hydrocarbons (alkenes), and 35% aromatic hydrocarbons (including alkylbenzenes and 2-, 3-ring aromatics) (Air Force 1989). Fuel oil #2 contains less than 5% polycyclic aromatic hydrocarbons (IARC 1989b). The typical hydrocarbon composition of fuel oil #2 is presented in Table E-4.b (Appendix E).

Fuel Oil #6. Fuel oil #6 is also called Bunker C or residual. It is the residual from crude oil after the light oils, gasoline, naphtha, fuel oil #l, and fuel oil #2 have been fractioned off. Fuel oil #6 can be blended directly to heavy fuel oil or made into asphalt. It is limited to commercial and industrial uses where sufficient heat is available to fluidize the oil for pumping and combustion (ABB Environmental 1990).

Residual fuel oils are generally more complex in composition and impurities than distillate fuels. Limited data are available on the composition of fuel oil #6 (ATSDR 1995g). Clark et al. (1990) indicate that fuel oil #6 includes about 25% aromatics, 15% paraffins, 45% naphthenes, and 15% non-hydrocarbon compounds. Polycyclic aromatic hydrocarbons (PAHs) and alkyl PAHs and metals are important hazardous and persistent components of fuel oil #6. Table E-4.b (Appendix E) presents the results of an analysis of one sample (Pancirov and Brown 1975).

Mineral Oils, Including Mineral-based Crankcase Oil. Mineral oils are often lubricating oils, but they also have medicinal and food uses. A major type of hydraulic fluid is the mineral oil class of hydraulic fluids (ATSDR 1997b). The mineral-based oils are produced from heavy-end crude oil distillates. Distillate streams may be treated in several ways, such as vacuum-, solvent-, acid-, or hydro- treated, to produce oils with commercial properties. Hydrocarbon numbers ranging from C_{15} to C_{50} are found in the various types of mineral oils, with the heavier distillates having higher percentages of the higher carbon number compounds (IARC 1984).

Crankcase oil or motor oil may be either mineral-based or synthetic. The mineral-based oils are more widely used than the synthetic oils and may be used in automotive engines, railroad and truck diesel engines, marine equipment, jet and other aircraft engines, and most small 2- and 4-stroke engines.

The mineral-based oils contain hundreds to thousands of hydrocarbon compounds, including a substantial fraction of nitrogen- and sulfur-containing compounds. The hydrocarbons are mainly mixtures of straight and branched chain hydrocarbons (alkanes), cycloalkanes, and aromatic hydrocarbons. PAHs, alkyl PAHs, and metals are important components of motor oils and crankcase oils, with the used oils typically having higher concentrations than the new unused oils. Typical carbon number chain lengths range from C_{15} to C_{50} (ABB Environmental 1990).

Because of the wide range of uses and the potential for close contact with the engine to alter oil composition, the exact composition of crankcase oil/motor oil has not been specifically defined. Table E-5.b (Appendix E) presents analytical results for some constituents in used automotive oil (ABB Environmental 1990).

3.3 ANALYTICAL METHODS

The purpose of this section is to describe well established analytical methods that are available for detecting, and/or measuring, and/or monitoring TPH and its metabolites, as well as other biomarkers of exposure and effect of TPH. The intent is not to provide an exhaustive list of analytical methods. Rather, the intention is to identify well-established methods that are used as the standard methods approved by federal agencies and organizations such as EPA and the National Institute for Occupational Safety and Health (NIOSH) or methods prescribed by state governments for water and soil analysis. Other methods presented are those that are approved by groups such as ASTM.

The term “total petroleum hydrocarbons” (TPH) is generally used to describe the measurable amount of petroleum-based hydrocarbons in the environment; and thus the TPH information obtained depends on the analytical method used. One of the difficulties with TPH analysis is that the scope of the methods varies greatly. Some methods are nonspecific while others provide results for hydrocarbons in a boiling point range. Interpretation of analytical results requires an understanding of how the determination was made.

Analytical methods for some petroleum products are discussed in existing ATSDR toxicological profiles. The very volatile gases (compounds with 4 carbons or less), crude oil, and the solid bituminous materials such as asphalt are not included in this discussion of analytical methods. ATSDR profiles relevant to petroleum products are listed in Table 3-1. The TPHCWG also addresses some of these issues from a different perspective which includes, in some cases, more detail and references than provided here (TPHCWG 1998a).

3.3.1 Environmental Samples.

Most of the analytical methods discussed here for TPH have been developed within the framework of federal and state regulatory initiatives. The initial implementation of the Federal Water Pollution Control Act (FWPCA) focused on controlling conventional pollutants such as oil and grease. Methods developed for monitoring wastewaters included EPA Method 4 13.1 (EPA 1979a) and EPA Method 413.2 (EPA 1979d) for Total Recoverable Oil and Grease (TOG), and EPA Method 418.1 for Total Recoverable Petroleum Hydrocarbons (TRPH) (EPA 1979c). Freon-extractable material is reported as TOG. Polar components may be removed by treatment with silica gel, and the material remaining, as determined by infrared (IR) spectrometry, is defined as Total Recoverable Petroleum Hydrocarbons (TPH, TRPH, or TPH-IR). A number of modifications of these methods exist. EPA Method 418.1 has been one of the most widely used methods for the determination of TPH in soils. Many states use, or permit the use of, EPA Method 418.1 for identification of petroleum products and during remediation of sites (George 1992; Judge et al. 1997, 1998). This method is subject to limitations, such as inter-laboratory variations and inherent inaccuracies (George 1992). In addition, the EPA proposed to withdraw wastewater methods which use Freon- 113 extraction (EPA 1996a). These methods will be replaced with EPA Method 1664: n-Hexane Extractable Material (HEM) and Silica Gel Treated *n*-Hexane Extractable Material (SGT-HEM) by Extraction and Gravimetry (Oil and Grease and Total Petroleum Hydrocarbons) (EPA 1996a). Conventional methods of TPH analysis are summarized in Table 3-2.

These conventional TPH analytical methods have been used widely to investigate sites that may be contaminated with petroleum hydrocarbon products. Many state and local regulatory agencies rely on and require EPA Method 418.1 (EPA 1979c) for determination of petroleum hydrocarbons (Murray 1994). The important advantages of this approach are (1) the method is relatively inexpensive, and (2) excellent sample reproducibility can be obtained. The disadvantages are (1) petroleum hydrocarbon composition varies among sources and over time, so results are not always comparable; (2) the more volatile compounds in gasoline and light fuel oil may be lost in the solvent concentration step; (3) there are inherent inaccuracies in the method; and (4) the method provides virtually no information on the types of hydrocarbons present. Several recent reports have detailed the problems with this approach (George 1992; Rhodes et al. 1995/1996). Thus, these conventional TPH methods, although they provide adequate screening information, do not provide sufficient information on the extent of the contamination and product type. In addition, The Clean Air Act Amendments of 1990 require the phaseout of the use of chlorofluorocarbons. Therefore, the EPA methods using Freon-l 13 will be replaced with EPA Method 1664, *n*-Hexane Extractable Material (HEM) and Silica Gel Treated *n*-Hexane Extractable Material (SGT-HEM) by Extraction and Gravimetry (EPA 1996a). Proposed Method 1664 includes thorough method quality control, but results may not equivalent to the current methods. Examples of TPH methods for environmental media are shown in Table 3-3.

Gas chromatography (GC) methods do provide some information about the product type. Most methods involve a sample preparation procedure followed by analysis using GC techniques. GC

Table 3-2. Summary of Conventional TPH Methods

Method name	Type	Matrix	Scope of method	Reference
Gravimetric methods				
EPA Method 413.1	TOG	Water and wastewater	Petroleum fuels from gasoline through #2 fuel oils are completely or partially lost in the solvent removal operation. Recoveries of some crude oils and heavy fuel oils will be low.	EPA 1979a
EPA Method 9070	TOG	Solid waste	Applicable to determination of relatively nonvolatile hydrocarbons. Not applicable to measurement of light hydrocarbons; petroleum fuels, from gasoline through No. 2 fuel oils, are completely or partially lost. Recoveries of some crude oils and heavy fuel oils will be low.	EPA 1995d
EPA Method 9071A	TOG	Sludge	Used to recover low levels of oil and grease from sludge. Used when relatively polar, heavy petroleum fractions are present, or when the levels of nonvolatile greases challenge the solubility limit of the solvent. Not recommended for measurement of low-boiling fractions.	EPA 1995d
Standard Method 5520B	TOG	Water and wastewater	Suitable for biological lipids and mineral hydrocarbons. Not suitable for low-boiling fractions.	APHA 1992
Standard Method 5520D	TOG	Water and wastewater	Suitable for biological lipids and mineral hydrocarbons. Method D is the method of choice when relatively polar, heavy petroleum fractions are present, or when the levels of nonvolatile greases may challenge the solubility of the solvent	APHA 1992
Standard Method 5520E	TOG	Sludges	Suitable for biological lipids and mineral hydrocarbons. Not suitable for low-boiling fractions. Method E is a modification of Method D.	APHA 1992
Standard Method 5520F	TPH	Water and wastewater	Suitable for biological lipids and mineral hydrocarbons. Not suitable for low-boiling fractions. May be used in conjunction with Method B, D or E.	APHA 1992
Infrared methods				
EPA Method 413.2	TOG	Water and wastewater	Applicable to the measurement of light fuels, although loss of about half of any gasoline present during the extraction manipulation can be expected	EPA 1979c

Table 3-2. Summary of Conventional TPH Methods (continued)

Method name	Type	Matrix	Scope of method	Reference
EPA Method 418.1	TPH	Water and wastewater	Applicable to a wide range of hydrocarbons, although volatile components will be lost. Modifications exist for measurement of TPH in soil.	EPA 1979c
Standard Method 5520C	TOG	Water and wastewater	Suitable for biological lipids and mineral hydrocarbons. The lighter distillates, with the exception of gasoline, may be measured accurately. Method C is the method of choice for low levels of oil and grease.	APHA 1992

TOG = (Total) oil and grease; TPH = Total Petroleum Hydrocarbons.

Table 3-3. Analytical Methods for Determining Total Petroleum Hydrocarbons in Environmental Samples

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Occupational air (hydrocarbons, BP=36–126 °C)	Sample collection on solvent tubes; solvent desorption	GC/FID	0.001 to 0.01 mg per sample[a]	>75[b]	NIOSH 1994 (Method 1500)
Ambient air	None	Continuous sampling/FID	0.16 ppm (0.1 mg/m^3)	Not reported	Lodge 1988 (ISC Method 108)
Ambient air	Collection on Tenax GC cartridge; thermal desorption	Capillary GC/MS	~20 ng injected	Not reported	EPA 1988 (Method TO-1)
Water, wastes (Oil and grease)	Solvent extraction	Gravimetric			EPA 1979e (Method 413.1)
Water, wastes (Oil and grease)	Solvent extraction	IR	~0.2 mg/L	99	EPA 1979d (Method 413.2)
Water and wastes (TRPH)	Solvent extraction; silica gel column separation	IR	≤1 mg/L		EPA 1979c (Method 418.1)
Water, aqueous wastes (oil and grease)	Solvent extraction	Gravimetric	5 mg/L	93	EPA 1988a (Method 9070)
Sludge and sediment (oil and grease)	Sample is dried; Soxhlet extraction	Gravimetric	10 mg/L	93	EPA 1988a (Method 9071A)
Soils, sediments, fly ash (TRPH)	Supercritical fluid extraction	Method 8015B	See Method 8015B	See Method 8015B	EPA 1995d (Method 3560)
Soil (TPH)	Extraction; filtration	Immunoassay	5.8 ppm	Not reported[d]	EPA 1995d (Method 4030)
Ground or surface water, soil (DRO, GRO)	DRO: solvent extraction; GRO: purge and trap or vacuum distillation or headspace sampling	Capillary GC/FID	DRO (low aromatic) ≤75 ppm; (regular)≤25 ppm	DRO: (low aromatic) 72–96; (regular) 125	EPA 1995d (Method 8015B)
Water (petroleum oils)	Solvent extraction; evaporation	GC/FID	Not reported[c]	Not reported[c]	ASTM 1994 (Method D 3328)
	Solvent extraction; evaporation	IR	Not reported[c]	Not reported[c]	ASTM 1994 (Method D 3414)

Table 3-3. Analytical Methods for Determining Total Petroleum Hydrocarbons in Environmental Samples (continued)

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Soils	Supercritical fluid extraction	IR		82.9	Lopez-Avila et al. 1993
Soils (gasoline and diesel)	Solvent extraction	Capillary GC/MSD-SIM	≤1 ppm	80–120	Xiang et al. 1995
Fish tissue (kerosene range)	Homogenization; digestion/solvent extraction	Capillary GC/FID	Low to sub-ppm	95	Guiney et al. 1987
Fish tissue	Solvent extraction; fractionation on silica gel columns; solvent exchange	GC/FID	Low ppm	90–113	Murray and Lockhart 1981
Avian tissue (liver, kidney, fat, brain tissue	Solvent extraction; saponification of fatty tissue; clean-up on adsorbent columns	Capillary GC/FID and GC/MS	ppb range	40–100 (target compounds)	Gay et al. 1980
Marine lipids (fish oils)	Saponification of lipids, followed by solvent extraction; cleanup on adsorbent columns or plates	GC/FID	Not reported[a]	Not reported[a]	Farrington et al. 1973
Mollusc tissue (TPH)	Homogenization; digestion and solvent extraction; fractionation on an adsorbent column	Capillary GC/FID	≈0.1 ppm	Not reported	Steimle et al 1986
Fish tissue, fish liver	Solvent extraction, followed by saponification of lipids; fractionation on adsorbent columns	Capillary GC/FID; confirmation by capillary GC/MS	Low ppm	Not reported	Fowler et al. 1993
Palm kernel oil (hydrocarbons)	Kernels ground, pressed, filtered; Soxhlet extraction of oil; fractionation on silica gel columns	GC/FID; identification of components by GC/MSD	≈1 μg/g	70–87	Tan and Kuntom 1994

[a] Actual detection limits will depend upon the volume of air sampled

[b] Desorption efficiency

[c] Method is qualitative; samples are compared to known petroleum oils

[d] Method 4030 provides an estimated of concentration

BP = boiling point; DRO = diesel range organics; GC = gas chromatography; GRO = gasoline range organics; FID = flame ionization detector; IR = infrared spectrophotometry; MS = mass spectrometry; MSD = mass selective detector; SIM = selected ion monitoring; TPH = total petroleum hydrocarbons; TRPH = total recoverable petroleum hydrocarbons determination is based on selected components or the sum of all components detected within a given range. Frequently the approach is to use two methods, one for the volatile range and another for the semivolatile range. Volatiles in water or solid samples are determined by purge-and-trap GC/FID. The analysis is often called the gasolines range organics (GRO) method. The semivolatile range is determined by analysis of an extract by GC/FID and is referred to as diesel range organics (DRO). Individual states have adopted methods for measuring GRO and DRO contamination in soil and water. The specific method details and requirements vary from state to state. Some of the GC TPH methods are summarized in Table 3-4.

In the mid-1980s underground storage tank (UST) programs were a focus of federal and state initiatives. The criteria and methodology for determining contamination are generally state-specific. Although many states still use EPA Method 418.1, GC procedures have been developed to provide more specific information on hydrocarbon content of waters and soils (Judge et al. 1997, 1998). GRO and DRO are specified in some cases, and several states, such as California and Wisconsin, aggressively developed programs to address groundwater contamination problems. These GC methods, coupled with specific extraction techniques, can provide information on product type by comparison of the chromatogram with standards. Quantitative estimates may be made for a boiling range or for a range of carbon numbers by summing peaks within a specific window. Although these methods provide more product information than the TPH and TOG methods, they are not without limitations. These include high results caused by interferences, low recovery due to the standard selected, petroleum product changes caused by volatility, and microbial activity (Restek 1994).

Many methods are available for analysis of petroleum hydrocarbon products, particularly in water and soil matrices. The current literature includes a number of studies that document the performance and limitations of the commonly used methods. Method modifications and new methods are being investigated to provide better information about the petroleum component content of environmental samples. However, the available analytical methodology alone may not provide adequate information for those who evaluate the movement of petroleum components in the environment or evaluate the health risks posed to humans (Heath et al. 1993a).

In its work to develop a fraction approach to assess TPH risks the TPH Criteria Working Group (TPHCWG) has developed an analytical method for identifying and quantifying the presence of the

Table 3-4. Summary of Gas Chromatographic TPH Methods

Method name	Matrix	Scope of method	Reference
Direct injection methods			
EPA Method 8015B	Solid wastes	Used to determine the concentration of petroleum hydrocarbons, including gasoline range organics (GROs). Analysts should use the fuel contaminating the site for quantitation.	EPA 1995c
ASTM Method D3328-90	Water	Petroleum oils such as distilate fuel, lubricating oil, and crude oil recovered from water or beaches. Identification of a recovered oil is determined by comparison with known oils, selected because of their possible relationship to the recovered oil.	ASTM 1994
Purge and trap and headspace methods			
EPA Method 8015B	Solid wastes	Used to determine the concentration of petroleum hydrocarbons, including diesel range organics (DROs) and jet fuel. Analysts should use the fuel contaminating the site for quantitation.	EPA 1995c

[a] Qualitative, screening procedur

DRO = diesel range organics; GRO = gasoline range organics; TPH = total petroleum hydrocarbons groups or fractions with similar mobility in soils. The technique is based on EPA Method 3611 (Alumina Column Cleanup and Separation of Petroleum Wastes) and EPA Method 3630 (Silica Gel Cleanup), which are used to fractionate the hydrocarbon into aliphatic and aromatic fractions. A gas chromatograph equipped with a boiling point column (non-polar capillary column) is used to analyze whole soil samples as well as the aliphatic and aromatic fractions to resolve and quantify the fate-and-transport fractions selected by the TPHCWG (Gustafson 1997). The method is versatile and performance-based and, therefore, can be modified to accommodate data quality objectives (Gustafson 1997).

The Massachusetts Department of Environmental Protection (MADEP) approached its needs to evaluate the potential health effects of petroleum hydrocarbons similarly by defining analytical fractions. MADEP's method is based on standard EPA Methods (8020/8015 Modified), which allows it to be easily implemented by contract laboratories (Gustafson 1997; Hutcheson et al. 1996). Lighter hydrocarbon fractions (C_6-C_{12} are analyzed by purge-and-trap GC analysis using a FID to measure the total hydrocarbons and a photoionization detector (PID) to measure the aromatics. The aliphatic (e.g., hexane) component of the TPH is found by determining the difference. Aromatic and aliphatic fractions are divided into carbon number fractions based on the normal alkanes (e.g., *n*-octane) as markers. Heavier hydrocarbons (C_{12}-C_{26}) are analyzed using an extraction procedure followed by a column separation using silica gel (Modified EPA Method 3630) of the aromatic and aliphatic groupings or fractions. The two fractions are then analyzed using GC/FID. PAH markers and *n*-alkane markers are used to divide the heavier aromatic and aliphatic fractions by carbon number, respectively. A couple of concerns about the methodology have been expressed: (1) the PID is not completely selective for aromatics and can lead to an overestimate of the more mobile and toxic aromatic content; and (2) the results from the two analyses, purgeable and extractable hydrocarbons, can overlap in carbon number and cannot be simply added together to get a total TPH concentration.

Few methods are available for monitoring petroleum products in other matrices such as plant and animal tissue and food.

3.3.1.1 Soils and Sediments

Methods for determining TPH in soils and sediments are discussed in Section 3.3.1 above. These methods are used primarily for UST programs. Currently, many of the states have adopted EPA Method 418.1 or modified EPA Method 801.5 or similar methods for analysis during remediation of contaminated sites. Thus, there is no standard for TPH analysis; each state has adopted its own criteria, and in some cases, developed its own methodologies (Murray 1994).

There is a trend toward use of GC techniques in analysis of soils and sediments. One aspect of these methods is that "volatiles" and "semivolatiles" are determined separately. The volatile or GRO components are recovered using purge-and-trap or other stripping techniques (Chang et al. 1992; EPA 1995d; McDonald et al. 1984). Semivolatiles are separated from the solid matrix by solvent extraction (EPA 1995d). Other extraction techniques have been developed to reduce the hazards and the cost of solvent use and to automate the process (Gere et al. 1993). Techniques include supercritical fluid extraction (SFE) (Fitzpatrick and Tan 1993; Gere et al. 1993; Hawthorne et al. 1993; Lopez-Avila et al. 1993) microwave extraction (Hasty and Revesz 1995; Lopez-Avila et al. 1994) Soxhlet extraction (Martin 1992) sonication extraction (Martin 1992) and solid phase extraction (SPE) (Schrynemeeckers 1993). Capillary column techniques have largely replaced the use of packed columns for analysis, as they provide resolution of a greater number of hydrocarbon compounds.

3.3.1.2 Water and Waste Water

Methods for determining TPH in aqueous samples are discussed above in Section 3.3.1. The overall method includes sample collection and storage, extraction, and analysis steps. Sampling strategy is an important step in the overall process. Care must be taken to assure that the samples collected are representative of the environmental medium and that they are collected without contamination. There are numerous modifications of the EPA, American Public Health Association (APHA), and American Society for Testing and Materials (ASTM) methods discussed above. Most involve alternate extraction methods developed to improve overall method performance for TPH or replacement of the chlorofluorocarbon solvents. SPE techniques have been applied to water samples (Schrynemeeckers 1993). Solvent extraction methods with hexane (Murray and Lockhart 1981; Picer and Picer 1993) or methylene chloride (Mushrush et al. 1994) have been reported as well.

3.3.1.3 Air

Methods for determining hydrocarbons in air matrices usually depend upon adsorption of TPH components onto a solid sorbent, subsequent desorption and determination by GC techniques. Hydrocarbons within a specific boiling range (*n*-pentane through *n*-octane) in occupational air are collected on a sorbent tube, desorbed with solvent, and determined using GC/FID (NIOSH 1994). Although method precision and accuracy are good, performance is reduced at high humidity.

Compounds in the boiling range 80-200 ºC in ambient air may be captured on a Tenax GC adsorbent tube which is thermally desorbed for GC/MS analysis (EPA 1988). Performance of the method had not been established on a compound-by-compound basis (EPA 1988). Gasoline vapor in air may be sampled on a tube containing Tenax adsorbent. The traps are thermally desorbed and analyzed by GC/FID. The minimum detectable concentration is 0.03 mg/m^3 total hydrocarbons in a 2.5 L sample. Excellent recovery was reported (>90%) (CONCAWE 1986). Passive adsorbent monitors (badges) may also be used. Compounds are solvent-desorbed from the exposed adsorbent and analyzed by GC. Good recovery (>80%) has been reported for target *n*-alkanes and for gasoline, naphtha, and Stoddard solvent (3M 1993).

The Massachusetts Department of Environmental Protection (MADEP), along with ENRS, Inc., of Acton, Massachusetts, has developed a method for taking and analyzing air samples for the presence of petroleum hydrocarbons (MADEP 1999). This Air-phase Petroleum Hydrocarbon (APH) method uses SUMMA canisters and GC/MS for sampling and analysis of ambient air, indoor air, and soil gas. This method can be downloaded from the MADEP website (http://www.state.ma.us/dep). The complex mixture of petroleum hydrocarbons potentially present in an air sample is separated into aliphatic and aromatic fractions, and then these two major fractions are separated into smaller fractions based on carbon number. Individual compounds (e.g., benzene, toluene, ethylbenzene, xylenes, MTBE, naphthalene) are also identified using this method. The range of compounds that can be identified includes C4 (1,3-butadiene) through C 12 (*n*-dodecane).

Continuous monitoring systems for total hydrocarbons in ambient air are available. These usually involve flame ionization detection. Detection limits are approximately 0.16 ppm (Lodge 1988).

3.3.2 Biological Samples

Few analytical methods were located for determination of TPH in biological samples. However, analytical methods for several important hydrocarbon components of total petroleum hydrocarbons may be found in the ATSDR toxicological profiles listed in Table 3-1.

Some methods developed for analysis of aquatic and terrestrial life may be adaptable to human biological samples. Examples are summarized in Table 3-5. Most involve solvent extraction and saponification of lipids, followed by separation into aliphatic and aromatic fractions on adsorption columns. Hydrocarbon groups or target compounds are determined by GC/FID or GC/MS. These methods may not be suitable for all applications, so the analyst must verify the method performance prior to use.

Methods are also available for determination of specific hydrocarbon compounds in biological samples. Some of these methods are shown in Table 3-5. Since these methods have not been demon- strated for total petroleum hydrocarbons, the analyst must verify that they are suitable prior to use.

3.3.3 Adequacy of the Database

Section 104(i)(5) of CERCLA, as amended, directs the Administrator of ATSDR (in consultation with the Administrator of EPA and agencies and programs of the Public Health Service) to assess whether adequate information on the health effects of TPH is available. Where adequate information is not available, ATSDR, in conjunction with the NTP, is required to assure the initiation of a program of research to determine the health effects (and techniques for developing methods to determine the health effects) of TPH. Since TPH is comprised of a number of component chemicals, these directives and requirements can be assumed to extend to the individual compounds that may be found as components of TPH.

Health assessment of the risks associated with petroleum hydrocarbons from environmental media are difficult because of the complex nature of petroleum products, lack of adequate knowledge about the movement of petroleum components in soil, and lack of knowledge about the toxicity of the components (Heath et al. 1993a). Health assessors often select surrogate or reference compounds (or combinations of compounds) to represent TPH so that toxicity and environmental fate can be

Table 3-5. Analytical Methods for Determining Total Petroleum Hydrocarbons in Biological Samples

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Human milk (purgeable hydrocarbons)	Purge and trap; thermal desorption	Capillary GC/MS	Not reported	35–88[a]	Pellizzari et al. 1982
Blood	Heated headspace extraction	Capillary GC/MS-SIM	50 picograms injected	No data	Kimura et al. 1991
Blood	Purge and trap	Isotope dilution: capillary GC/high resolution MS	Low ppt	91–147	Ashley et al. 1992
Breath	Collection in passivated cannisters using spirometer system	Capillary GC/MS	Low μg/m^3 range	25–136	Thomas et al. 1991

[a] Data for 4 control compounds

FID = flame ionization detector; GC = gas chromatography; MS = mass spectrometry; TPH = total petroleum hydrocarbons evaluated. One approach is based on benzene as the most appropriate substitute for TPH based on its toxicity, motility in the environment, and solubility in ground water (Youngren et al. 1994). Other researchers have investigated the use of several surrogate compounds to represent the movement of TPH in the environment and TPH toxicity. Potential candidates are *n*-hexane, benzo(a)pyrene, and pyrene to represent alkanes, carcinogenic PAHs, and noncarcinogenic PAHs in gasoline, respectively. Benzene and toluene would be included for sites where the BTEX portion of gasoline is not analyzed separately (Koblis et al. 1993).

Another approach is to categorize hydrocarbon compounds into surrogate fractions characterized by similar chemical and physical properties (EA Engineering 1995). Compounds are assigned to a given fraction on the basis of similar leaching and volatilization factors. Correlation to Carbon Number Index was used because it closely follows GC behavior. This method has the potential to provide realistic evaluation of potential risks; however, a full set of parameters is not available for all the compounds of interest (EA Engineering 1995).

3.3.4 Ongoing Studies

Governmental, industrial, and environmental groups have been attempting to understand the problems of environmental contamination with petroleum hydrocarbons. Major agencies, such as the International Agency for Research on Cancer (IARC) and the EPA are involved in the discussion of potential health effects. Some groups have been attempting to improve the analytical consistency and interpretation of results in dealing with petroleum hydrocarbons, and some have looked at the health and environmental effects of petroleum. The ASTM publishes consensus standards, including analytical methods. Committee D-19 of ASTM is concerned with the study of water and is responsible for the standardization of methods for sampling and analysis of water, aqueous wastes, water-formed deposits, and sediments. Committee D-2 on Petroleum Products and Lubricants is responsible for the ASTM *Manual on Hydrocarbon Analysis* (ASTM 1992).

The Amherst annual conference continues to address issues surrounding petroleum contamination, including analytical methods (Amherst 1999). Though the TPHCWG has taken on specific responsibilities for TPH, further analytical developments will likely grow from this conference.

In another ongoing effort, EPA is looking at the problem of petroleum wastes in all media. They have formed an internal working group and are supporting the efforts of other groups such as the Amherst Conference Workgroups and Workshop on General Population Exposures to Gasoline (Lioy 1992).

Dr. R.J. Rando, Tulane University, is investigating the use of passive samplers for measuring hydrocarbon components. The overall goal of the program is to characterize and improve the performance of passive samplers for use in ambient and indoor air monitoring.

Petroleum companies have conducted a number of studies regarding the health effects of TPH constituents and products that have not appeared in the open published literature (API 1995a).