STATE OF CONNECTICUT

DEPARTMENT OF ENERGY & ENVIRONMENTAL PROTECTION

SELECTION OF ANALYTICAL METHODS FOR PETROLEUM RELEASES

GUIDANCE DOCUMENT

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The Connecticut Department of Energy and Environmental Protection (DEEP) developed this guidance document to assist the environmental professional (EP) in the selection of analytical methods appropriate to any applicable data quality objectives (DQOs) to identify and quantify petroleum releases. This guidance was developed by the DEEP Remediation Division's Laboratory Quality Assurance/Quality Control Work Group (Work Group). The Work Group is comprised of licensed environmental professionals (LEPs), data validators, and representatives from private laboratories and DEEP. DEEP gratefully acknowledges the contributions and assistance of those individuals who volunteered their time and effort to help develop and prepare this document.

Petroleum products are a complex and highly variable mixture of individual hydrocarbons. To help bring about the end of Freon use in Connecticut and to be consistent with Federal Law, the DEEP does not accept analytical data derived by the United States Environmental Protection Agency (EPA) Method 418.1 for samples collected on or after June 30, 2009.

Releases of petroleum products may be identified and quantitated through the use of various methods appropriate to the necessary DQOs, in no order of preference, including, but not limited to:

- Extractable Total Petroleum Hydrocarbons (CT ETPH)
- Extractable Petroleum Hydrocarbons (EPH)
- Volatile Petroleum Hydrocarbons (VPH)
- Air-Phase Petroleum Hydrocarbons (APH)
- Method 8260
- Method 8270
- Method 524
- Method 525

This overview is designed to answer general questions and provide basic information. The information contained in this guidance document does not constitute the Department's interpretation of the applicable laws or best professional practices. The EP should refer to the appropriate statutes and regulations and comply with applicable laws. Nothing in this document should be viewed as limiting or obviating the need for the exercise of good professional judgment.

This document excludes radiological issues including, but not limited to, those described in Title 22a Chapters 446 and 446A that are overseen by the DEEP Monitoring and Radiation Division of the Bureau of Air Management. This document does not apply to Polychlorinated Biphenyls pursuant to the Title 40 Code of Federal Regulations (CFR) Part 761.

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200.8	EPA Method 200.8: Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma-Mass Spectrometry
505	EPA Method 505: Analysis of Organohalide Pesticides and Aroclors in Drinking Water by Microextraction and Gas Chromatography
508.1	EPA Method 508.1: Determination of Chlorinated Pesticides, Herbicides, and Organohalides by Liquid-solid Extraction and Electron Capture Gas Chromatography
524.2	EPA Method 524.2: Measurement of purgeable organic compounds in water by capillary column gas chromatography/mass spectrometry
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525.2	EPA Method 525.2: Determination of Organic Compounds in Drinking Water by Liquid-Solid Extraction and Capillary Column Gas Chromatography/Mass Spectrometry
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6010	EPA SW-846 Method 6010: Inductively Coupled Plasma-Atomic Emission Spectrometry
6020	EPA SW-846 Method 6020: Inductively Coupled Plasma – Mass Spectrometry
7000/7010	EPA SW-846 Method 7000: Flame Atomic Absorption Spectrophotometry EPA SW-846 Method 7010: Graphite Furnace Atomic Absorption Spectrophotometry
7196	EPA SW-846 Method 7196: Chromium, Hexavalent (Colorimetric)
7470/7471	EPA SW-846 Method 7470: Mercury in Liquid Wastes (Manual Cold-Vapor Technique)

EPA Method	Method Title
	EPA SW-846 Method 7471: Mercury in Solid or Semisolid Wastes (Manual Cold-Vapor Technique)
8082	EPA SW-846 Method 8082: Polychlorinated Biphenyls (PCBs) by Gas Chromatography
8260	EPA SW-846 Method 8260: Volatile Organic Compounds by Gas Chromatography-Mass Spectrometry (GC/MS)
8270	EPA SW-846 Method 8270: Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC-MS)
APH	MassDEP Air-Phase Petroleum Hydrocarbons
EPH	MassDEP Extractable Petroleum Hydrocarbons
ETPH	CT Extractable Total Petroleum Hydrocarbons
VPH	MassDEP Volatile Petroleum Hydrocarbons
TO-10A	Method TO-10A: Determination of Pesticides and Polychlorinated Biphenyls In Ambient Air Using Low Volume Polyurethane Foam (PUF) Sampling Followed By Gas Chromatographic/Multi-Detector Detection (GC/MD)
TO-13	Method TO-13A: Determination of Polycyclic Aromatic Hydrocarbons (PAHs) in Ambient Air Using Gas Chromatography/Mass Spectrometry (GC/MS)
TO-15	Method TO-15: Determination of Volatile Organic Compounds (VOCs) in Air Collected in Specially-Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS)
TO-17	Method TO-17: Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling Onto Sorbent Tubes

GLOSSARY

Acronym	Term	Definition
	Additive	Any compound added to the normal formulation of the specified product. For example, tetraethyl lead, ethylene dibromide (EDB), and later methyl-tert-butyl ether (MTBE) were additives to gasoline that are no longer used. Current additives, which are added to gasoline to boost the octane level, include tertiary butyl alcohol (TBA), ethanol, tert-Amyl methyl ether (TAME), and others.
APH	Air-Phase Petroleum Hydrocarbons	Air-Phase Petroleum Hydrocarbons (APH) are defined as collective ranges of hydrocarbon compounds eluting from isopentane to n-dodecane, excluding Target APH Analytes. APH is comprised of C5-C8 aliphatic hydrocarbons, C9-C12 aliphatic hydrocarbons, and C9-C10 aromatic hydrocarbons.
	Aliphatic Hydrocarbon	A straight-chain hydrocarbon compound consisting of hydrogen and carbon only.
	Analytical Method	Laboratory method or technique used to determine the concentration of a compound, chemical element, or group of compounds.
PCB Aroclors	Aroclors	Commercial mixes of man-made class of chemicals known as polychlorinated biphenyls (PCB).
	Aromatic Hydrocarbon	A compound which contains one or more benzene rings.
	Carbon Range	The range in which compounds elute in a given retention-time window as defined by method-specified markers. For example, the C9 to C12 aliphatic carbon range refers to compounds that elute in the retention time between nonane (C9) and dodecane (C12).

Acronym	Term	Definition
CFR	Code of Federal Regulations	The codification of the general and permanent rules published by the Federal Register by the departments and agencies of the Federal Government.
CSM	Conceptual Site Model	Defined in *State of Connecticut, Department of Energy Environmental Protection, Release Characterization Guidance,* effective December 15, 2025, and as may be amended from time to time.
	Congeners	Specific PCB compounds that are made of two bonded phenyl (aromatic carbon) rings that have at least one hydrogen ion substituted with a chlorine atom. There are 209 distinct PCB congeners.
CVAA	Cold Vapor Atomic Absorption	A sensitive, specialized spectroscopy analytical technique used primarily to measure trace levels of mercury in various environmental matrices.
DEEP	Connecticut Department of Energy and Environmental Protection	
DPH	Connecticut Department of Public Health	
DQOs	Data Quality Objectives	Defined in the *State of Connecticut, Department of Energy and Environmental Protection, Release Characterization Guidance (RCG),* effective March 1, 2026, and as may be amended from time to time.
EDB	Ethylene dibromide	A chemical compound that was historically used as an additive to leaded gasoline and as a fumigant.

Acronym	Term	Definition
EP	Environmental Professional	An individual who has specific education, training, and experience necessary to exercise sound professional judgment to develop conclusions regarding conditions indicative of releases or potential releases at a site as defined in the *State of Connecticut, Department of Energy and Environmental Protection, Release Characterization Guidance (RCG),* effective March 1, 2026, and as may be amended from time to time.
EPA	United States Environmental Protection Agency	
EPH	Extractable Petroleum Hydrocarbons	Extractable Petroleum Hydrocarbons (EPH) are defined as collective ranges of hydrocarbon compounds eluting from n-nonane (C9) to n-hexatriacontane (C36), excluding target polycyclic aromatic hydrocarbons (PAH) Analytes. EPH is comprised of C9 through C18 aliphatic hydrocarbons, C19 through C36 aliphatic hydrocarbons, and C11 through C22 aromatic hydrocarbons, as reported by the Reasonable Confidence Protocol for Extractable Petroleum Hydrocarbons.
ETPH	Extractable Total Petroleum Hydrocarbons	See Regulations of Connecticut State Agencies (RCSA) Section 22a-134tt-1(a), hydrocarbons which elute within the C9 through C36 range, including aliphatic and aromatic hydrocarbons, as reported by the Reasonable Confidence Protocol for Extractable Total Petroleum Hydrocarbons.
FAAS	Flame Atomic Absorption Spectrometry	A spectrophotometric instrument that uses a high-temperature flame to atomize samples and measure absorption of specific light wavelengths to measure concentrations of metals.

Acronym	Term	Definition
GAAS	Graphite Atomic Absorption Spectrometry	A spectrophotometric instrument that uses a high-temperature graphite tube to atomize samples and measure absorption of specific light wavelengths to measure concentrations of metals.
GC	Gas Chromatography	A common form of chromatography used to characterize organic compounds. Gas chromatography methods employ a variety of detectors that respond to various classes of organic compounds aiding in determining the specific compound(s) present.
GC/MS	Gas Chromatography/Mass Spectrometry	Gas Chromatography/Mass Spectrometry is an analytical procedure in which a gas chromatograph is connected to a mass spectrometer. The technique allows for both accurate identification and quantitation of analytes.
ICP-MS	Inductively Couple Plasma-Mass Spectrometry	A highly sensitive analytical technique that ionizes samples using argon plasma and separates the resulting ions based on their mass-to-charge ratio using a mass spectrometer to detect trace concentrations of most elements.
ICP-OES	Inductively Coupled Plasma-Optical Electron Spectroscopy	A highly sensitive analytical technique that ionizes samples using argon plasma. The argon plasma excites the ions causing them to emit light at characteristic wavelengths.
	Indicator Compounds	Compounds which are commonly indicative of a specific class of petroleum products.
LEP	Licensed Environmental Professional	See RCSA 22a-134tt-1(a).
MTBE	Methyl-tert-butyl-ether	A chemical compound historically used as an additive in gasoline.

Acronym	Term	Definition
	Oxygenates	Compounds which are added to fuels to increase oxygen content, such as the additive compound ethanol.
PAHs	Polycyclic Aromatic Hydrocarbons	AKA Polynuclear Aromatic Hydrocarbons. Class of organic compounds composed of two, or more, biphenyl rings. May contain various organic functional groups.
PCBs	Polychlorinated biphenyls	A class of organic compounds composed of two, or more, biphenyl rings and one, or more, chlorine atoms used for various industrial applications.
	Petroleum	Petroleum is used in this document as the term is defined in Section 22a-449a of the Connecticut General Statutes.
	Purge and Trap	A dynamic headspace technique, used to extract, concentrate, and analyze volatile organic compounds (VOCs) from soli or liquid matrices.
QA Workgroup		Connecticut Department of Environmental Protection Remediation Division Laboratory Quality Assurance Quality Control Work Group
RBCRs	Release Based Cleanup Regulations	Regulations of RCSA Sections 22a-134tt-1 to 22a-134-App-12, inclusive.
RCG	*Release Characterization Guidance*	The RCG is designed to assist the environmental professional in constructing a conceptual site model (CSM) for an identified release, historical or emergent, and conducting environmental investigations to support and refine the CSM as they develop an understanding of the release and the distribution of related contaminants in the environment.
RCSA	Regulations of Connecticut State Agencies	

Acronym	Term	Definition
RCPs	Reasonable Confidence Protocols	See RCSA 22a-134tt-1(a).
	Release	Defined in the RBCRs, RCSA Section 22a-134tt-1(a) and in the *State of Connecticut, Department of Energy and Environmental Protection, Release Characterization Guidance (RCG),* effective March 1, 2026, and as may be amended from time to time.
RL/LLOQ	Reporting Limit / Lower Limit of Quantitation	Reporting limit / lower limit of quantitation (RL/LLOQ) means the concentration of the lowest non-zero calibration standard of a calibration curve used for analysis of a given sample by a specific method, corrected for specific sample weight or volume, dilutions, and for soil and sediment samples moisture content. This term is further defined in the RBCRs, RSCA Section 22a-134tt-1(a).
SIM	Selected Ion Monitoring	Refers to the use of the instrument to record the ion current at selected masses that are characteristic of the compound of interest in an expected retention time window.
SVOCs	Semi-Volatile Organic Compounds	A class of organic compounds that are more likely to be liquids or solids at ambient, or lower, temperatures.
TAME	Tert-amyl methyl ether	A chemical compound historically used as an additive to gasoline.
	Target Analytes	Target analytes are the compounds included on the list of analytes for an analytical method.
TBA	Tertiary butyl alcohol	A chemical compound used as a solvent and gasoline oxygenate, amongst other industrial applications.
VOCs	Volatile Organic Compounds	A class of organic compounds that have a high vapor pressure at room temperature, i.e., are commonly in the gaseous state at room temperature.

Acronym	Term	Definition
VPH	Volatile Petroleum Hydrocarbons	Volatile Petroleum Hydrocarbons (VPH) are defined as collective ranges of hydrocarbon compounds eluting from n-pentane (C5) to naphthalene, excluding Target VPH Analytes. VPH is comprised of C5 through C8 aliphatic hydrocarbons, C9 through C12 aliphatic hydrocarbons, and C9 through C10 aromatic hydrocarbons, as reported by the Reasonable Confidence Protocol for Volatile Petroleum Hydrocarbons.
VPS	Volatile Petroleum Substance	See RCSA section 22a-134tt-1(a).

1. INTRODUCTION

The purpose of this document is to provide information to assist the EP in the selection of analytical method(s) appropriate to applicable DQOs to identify and quantitate petroleum releases. This document intends to present information regarding these methods but does not intend to infer a preference of method(s) for a particular type of release. There may be other available methods than the methods included in this document.

Understanding the types of analytical methods available to identify and quantitate petroleum releases is important because petroleum releases are common. Many releases reported to the Department of Energy and Environmental Protection's (DEEP) Oil and Chemical Spill Response Division are petroleum releases.

Petroleum products:

- Include fuels, biofuels, some synthetic oils and naturally occurring hydrocarbons;
- Are highly variable mixtures resulting in different physical, chemical, and toxicological properties based on the substances present; and
- May also include additives.

2. SELECTING ANALYTICAL METHODS FOR IDENTIFICATION AND QUANTITATION OF PETROLEUM RELEASES

It is the responsibility of the EP to select appropriate analytical methods based on the nature of the release, site history, and the capability of the analytical methods to detect and to adequately evaluate the known or potential releases at a site based on DQOs necessary for the intended use of the data. Should the EP need assistance with selecting the appropriate method for applicable DQOs, the EP should consult the conceptual site model (CSM), seek peer review, or consult with knowledgeable experts.

Petroleum is a mixture of hundreds of hydrocarbon compounds, the majority of which have little toxicological data available. However, it has been observed that, in general:

- Petroleum products are comprised mainly of aliphatic and aromatic hydrocarbon compounds;
- Aromatic hydrocarbons are generally more toxic than aliphatic compounds; and
- The toxicity of aliphatic compounds is generally related to their carbon number/molecular weights.

The ETPH Method measures total extractable petroleum hydrocarbons with the number of carbons per compound ranging from C9 to C36. The method results in one concentration for the entire range. The EPH and VPH methods were developed to assist the EP in characterizing petroleum releases by breaking down the broad carbon range from C5 to C36 into specific ranges of aliphatic and aromatic hydrocarbons. These defined ranges of aliphatic and aromatic hydrocarbons established in the EPH and VPH methods were based on available toxicological data in relation to **non-cancer** reference doses.

The APH method was designed to better characterize petroleum releases in air by breaking down the volatile carbon ranges from C5 to C12 into specific ranges of aliphatic and aromatic hydrocarbons.

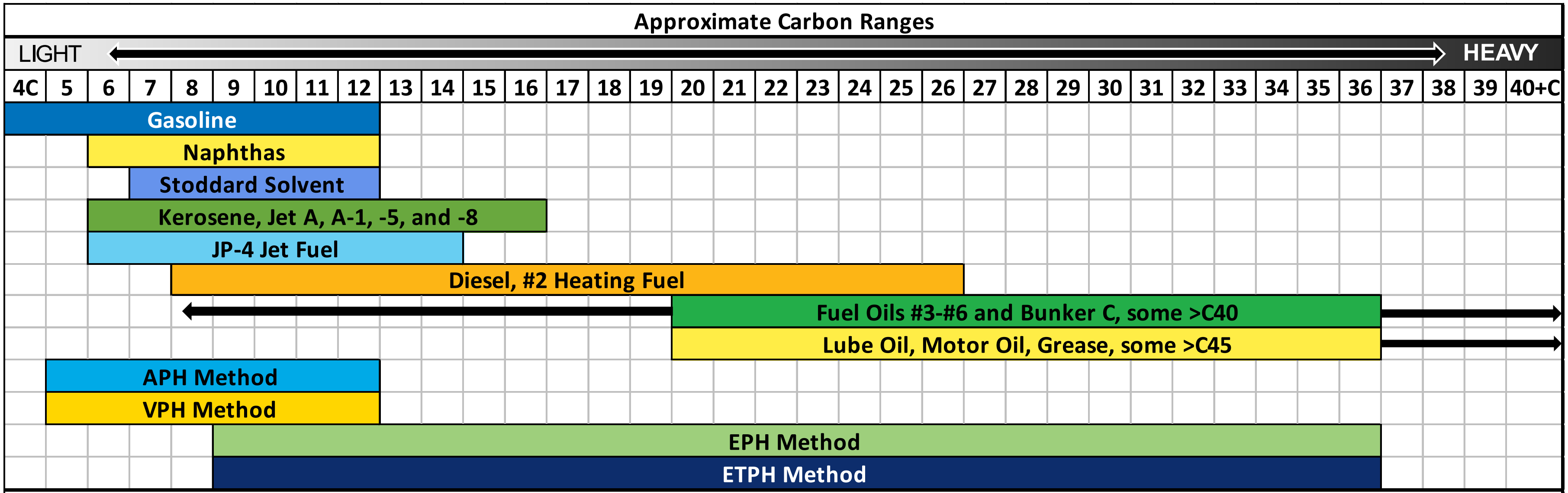
2.1 Considerations for Selecting a Method

Method selection should take into consideration:

- The intended use of the data, i.e., submitting data for characterization or demonstrating compliance;
- Suspected constituents of concern associated with the release;
- Potential to be the most appropriate indicators of a release and/or the need for remediation (depending on DQOs, e.g., Phase II versus Phase III DQOs);
- Transformations or weathering of contaminants that might occur over time or in response to geochemical changes in the subsurface;
- Type of release: It is more important to consider the type of release than age when determining analytical method(s). Because age may change the composition, location, and distribution of the petroleum hydrocarbons in the subsurface, the age of the release is important in development of the CSM; and

- Composition of the hydrocarbons at the time of release, e.g., leaded gasoline, polychlorinated biphenyls (PCBs) in oils, etc.

Figure 1 illustrates the carbon ranges for various petroleum products and the carbon ranges included in the analytical methods described in this document. Available analytical methods for various types of releases are described for soil, sediment, and aqueous matrices in Table 1 and for air and soil vapor in Table 2. The information provided in Figure 1 and Tables 1 and 2 is provided to assist the EP with selecting the available analytical method to identify and quantitate a release.



Notes:

Carbon ranges can vary from those depicted in this figure based on production processes and/or weathering.

Reference for carbon ranges - Analysis of Petroleum Hydrocarbons in Environmental Media, Total Petroleum Criteria Workgroup Series, Vols 1-2, 1998

Analytical carbon ranges derived from MassDEP Method and/or Reasonable Confidence Protocol for each method

Figure 1: Example of approximate carbon ranges for various petroleum hydrocarbon products and petroleum-specific analytical methods. Carbon ranges in samples can regularly change due to naturally occurring degradation/transformations of petroleum compounds, cross-contamination, or changes in proprietary formulas. This figure is not meant to be used to identify carbon ranges for the purposes of demonstrating compliance.

Table 1: Analytical Methods for Identification and Quantitation of Petroleum Releases in Soil, Sediment and Aqueous Matrices[1]

Petroleum Product Released	Analytical Methods for Identifying and Quantitating Releases *For Non-Potable and Solid Matrices*	Analytical Methods for Identifying and Quantitating Releases *For Potable Samples*	Comments
Gasoline, Light Petroleum Solvents[3] (Naphtha, Stoddard Solvent, mineral spirits, paint thinner, etc.)	8260 or[2] VPH (carbon ranges and target compounds) or[2] VPH (carbon ranges only) **and** 8260	Samples from water supply wells should be analyzed using EPA drinking water Methods 524.2/3 for volatile organic compounds (VOCs).	Consider analysis for the following oxygenates/additives on a site-specific basis: ethanol, tert-butyl alcohol (TBA), ethyl-tert-butyl-ether, tert-amyl methyl ether (TAME), 1,2-dichloroethane, di-isopropyl ether, methyl tert-butyl ether (MTBE), lead, and other fuel additives, such as ethylene dibromide (EDB), based on the CSM.
Jet Fuels, Kerosene, #2 Fuel Oil, Diesel[3]	8260, 8270 PAHs, and ETPH or[2] VPH (carbon ranges and target compounds), 8270 PAHs, **and** ETPH or[2] EPH and VPH (carbon ranges and target compounds for each method)	Samples from water supply wells should be analyzed using EPA drinking water Methods 524.2/3 for VOCs and 525.2/3 for polycyclic aromatic hydrocarbons (PAHs).	It may be appropriate to analyze for the full analyte list of 8270 (acids and base/ neutrals), not just PAHs.

Petroleum Product Released	**Analytical Methods for Identifying and Quantitating Releases** ***For Non-Potable and Solid Matrices***	**Analytical Methods for Identifying and Quantitating Releases** ***For Potable Samples***	**Comments**
#3 - #6 Fuel Oils, Lubricating Oils, Motor Oils, and Hydraulic Oils[3]	ETPH and 8270 PAHs <u>or</u>[2] EPH (carbon ranges and target compounds)	Samples from water supply wells should be analyzed using EPA drinking water Method 525.2/3 for PAHs.	It may be appropriate to analyze for the full analyte list of 8270 (acids and base/ neutrals), not just PAHs. Include testing for metals based on the CSM; include metals worn off during manufacturing processes or due to operation of equipment/machinery.[4]
Waste Oils, Used Oils and Unknown Petroleum Substances[3]	8260, 8270, ETPH, metals, 8082, <u>**and**</u> VPH (carbon ranges only for VPH) <u>or</u>[2] 8260, 8270, metals, 8082, VPH <u>**and**</u> EPH (carbon ranges only for VPH/EPH)	Samples from water supply wells should be analyzed using EPA drinking water Methods 524.2/3 for VOCs, 525.2/3 for semi-volatile organic compounds (SVOCs), 200.7/8 for metals, and 505/508.1/525.2/3 for PCBs (samples from water supply wells that need to be tested for PCBs may have more difficulty achieving the required RL/LLOQs if using EPA Method 505).	Full analyte list of 8260 (volatiles) Full analyte list of 8270 (acids and base/ neutrals) Consider analysis for the following oxygenates/additives on a site-specific basis: ethanol, TBA, ethyl-tert-butyl-ether, TAME, 1,2-dichloroethane, di-isopropyl ether, MTBE, lead, and other fuel additives, such as EDB, based on the CSM.

Petroleum Product Released	**Analytical Methods for Identifying and Quantitating Releases** ***For Non-Potable and Solid Matrices***	**Analytical Methods for Identifying and Quantitating Releases** ***For Potable Samples***	**Comments**
Transformer Oils, Mineral Oils and Dielectric Fluids	EPH (carbon ranges and target compounds) **and** PCBs by 8082 or[2] ETPH, 8270, and PCBs by 8082	Samples from water supply wells should be analyzed using EPA drinking water Method 525.2/3 for SVOCs.	It may be appropriate to analyze a subset of the EPA Method 8270 analyte list (e.g., PAHs).

[1] See information regarding sampling and analytical methods for Underground Storage Tank Closure.

[2] The word “or” is used to present a list of other potential method combinations that can be used for characterization.

[3] Consider the CSM when selecting analytical methods as there may be other contaminants of concern that are not provided in this table and may be needed to characterize the release.

[4] Per Total Petroleum Hydrocarbon Criteria Working Group Series, Volume 2, 1998.

Table 2: Analytical Methods for Identification and Quantitation of Petroleum Releases in Air and Soil Vapor[1]

Petroleum Product Released	Analytical Methods for Identifying and Quantitating Releases	Comments
Gasoline, Light Petroleum Solvents (naphtha, Stoddard Solvent, mineral spirits, paint thinner, etc.)	APH (carbon ranges and target compounds) or[2] TO-15 or[2] TO-17[3]	Consider analysis for the following oxygenates/additives on a site-specific basis: ethanol, TBA, ethyl-tert-butyl-ether, TAME, 1,2- dichloroethane, di-isopropyl ether, MTBE, lead, and other fuel additives, such as EDB, based on the CSM. For the APH Method or TO-15 Method, use silica-lined canisters to improve recovery.
Jet Fuels, Kerosene	APH (carbon ranges and target compounds) or[2] TO-15 or[2] TO-17[3]	For the APH Method or TO-15 Method use silica-lined canisters to improve recovery.
#2 Fuel Oil, Diesel	APH (carbon ranges and target compounds)	For the APH Method or TO-15 Method use silica-lined canisters to improve recovery.
#3 - #6 Fuel Oils, Lubricating Oils, and Hydraulic Oils	Consider analysis for APH when petroleum contamination may contain naphthalene in addition to any other site-specific contaminants. Consider analysis for TO-10A and/or TO-13 on a site-specific basis.	These "heavier" materials exhibit low vapor pressures and cannot be measured by the APH method.

Petroleum Product Released	**Analytical Methods for Identifying and Quantitating Releases**	**Comments**
Waste Oils, Used Oils, and Unknown Petroleum Substances	APH (carbon ranges and target compounds), TO-10A, TO-13, TO-15, TO-17[3], **and/or** oxygenates/additives on a site-specific basis.	If the CSM suggests that volatile non-petroleum compounds may have been released with petroleum products, analysis for those compounds in air should be considered.
Transformer Oils, Mineral Oils and Dielectric Fluids	TO-10A and/or TO-13 on a site-specific basis.	These "heavier" materials exhibit low vapor pressures and cannot be measured by the APH method.

[1] See information regarding sampling and analytical methods for Underground Storage Tank Closure.

[2] The word "or" is used to present a list of other potential method combinations that can be used for characterization.

[3] Use of Method TO-17 analysis is appropriate for the screening of petroleum releases. Due to limitations of the sorbent material identified in Method TO-17, analytical data resulting from a TO-17 analysis is not considered representative when demonstrating compliance with the Release Based Cleanup Regulations (RBCRs).

2.1.1 Considering Petroleum Additives When Selecting Analytical Methods

When considering the appropriate analytical methods to use to identify and quantitate a petroleum release, the EP should consider not only the petroleum hydrocarbons that may have been released but also any additives or other constituents that could have been associated with the petroleum product of interest. The EP should consider the site-specific CSM when deciding on the specific analyses that should be conducted for additives, recognizing that there may be gaps in the understanding of the site history that could affect the selection of analyses.

In evaluating whether to analyze for these constituents in addition to the petroleum hydrocarbons found in gasoline, the EP should take into consideration the timing of any gasoline releases at the property. A number of potential additives or additional compounds that could be associated with various types of petroleum releases are included in Tables 1 and 2. Oxygenates used primarily in gasoline may also be present in #2 fuel oil/ diesel or other non-gasoline petroleum products as tanks and pipelines may be used to store or transport different products at different times.

The following oxygenates/additives are provided as an example of the most commonly known compounds associated with gasoline, however, this list is subject to change over time: ethanol, TBA, ethyl-tert-butyl-ether, TAME, 1,2- dichloroethane, di-isopropyl ether, lead, MTBE, and other fuel additives, such as EDB, based on the CSM. Appropriate methods should be selected in consultation with the laboratory.

2.2 Data Quality Assessment and Data Useability Considerations

Due to the heterogeneity of environmental media, inherent variation in laboratory analytical methods, varying chemical composition (of petroleum products), matrix effects on analytical method performance, and human error potentially introduced during sampling, sample preparation and/or analysis, the results of analytical testing can include an element of uncertainty and may, in certain cases, introduce a bias. Accordingly, the EP should review laboratory data to assess its representativeness and identify biases, if found.

Understanding the representativeness and potential biases in any set of data is important since different analytical methods may produce several results for the same analyte. For example, benzene is a reported analyte by Method 8260 and as a target analyte by the VPH Method. Similarly, naphthalene is a reported analyte by Method 8260, Method 8270, and a target analyte by the VPH and EPH methods. Each of these methods have varying sensitivity, reporting limitations, and interferences because of differences in sample preparation and instrument methodology. In general, gas chromatography/mass spectrometry (GC/MS) methods are preferred for target analytes when results for the same compound exist. However, it is important for the EP to consider the intended purpose of the data and the DQOs required to meet those purposes.

The analytical methods referenced in this guidance document are used either to analyze for different individual analytes or to analyze for different suites of analytes. For example, Method 8260 only reports concentrations for individual analytes, whereas the VPH method can be used to analyze for both select individual analytes (which are a subset of the compounds reported by the EPA 8260 Method) and carbon ranges that are not reported by the EPA 8260 Method (a suite of analytes). Because of the differences in the methods, the results from one method are not directly comparable to the results from the other. As such, results from one method may better characterize a release than results from another. However, this is not just dependent on the method used but also the associated quality control results (e.g., surrogate recoveries, matrix spike recoveries, etc.).

If the EP has reason to believe that an analytical method, or suite of analytical methods, characterizes the release better than other methods, and as long as all data obtained are considered, then the rationale for using the results of that method must be thoroughly documented in the reports that use the data.

2.3 Reporting Limits / Lower Limits of Quantitation

Each of the referenced methods have different reporting limits / lower limits of quantitation (RL/LLOQ). Typical RL/LLOQs for each referenced method can be found in their respective Reasonable Confidence Protocols (RCPs). Certain methods may be capable of achieving RL/LLOQs that would either meet RBCR criteria, or be lower than RBCR criteria, without method modification for various environmental matrices. However, certain methods may require method modification to achieve lower RL/LLOQs necessary to achieve DQOs for the intended use of the data. In addition, sample matrices may occasionally contain constituents/materials that cause interferences in the analytical process resulting in elevated RL/LLOQs that exceed RBCR criteria. If a particular method cannot achieve desired RL/LLOQs then an alternative method may need to be utilized. For example, it may be necessary to utilize alternate methods such as Method 8270 selective ion monitoring (SIM) to achieve RL/LLOQs necessary for reporting target PAHs in water.

It is the responsibility of the data user, in concert with the laboratory, to establish the range and required RL/LLOQ for the target analytes to meet, or be lower than, RBCR criteria.

3. ANALYTICAL METHODS

The following subsections provide basic information on key analytical methods that are applicable to the analysis of petroleum hydrocarbons, particularly those identified in Tables 1 and Table 2. A list of references is also included in this document.

3.1 Analytical Methods

3.1.1 Extractable Total Petroleum Hydrocarbons

On June 22, 1999, the Commissioner of the State of Connecticut Department of Public Health (DPH) approved an analytical method for determination of ETPH. The method is titled "Analysis of Extractable Total Petroleum Hydrocarbons (ETPH Method) Using Methylene Chloride Gas Chromatograph/Flame Ionization Detection," prepared by the Environmental Research Institute, University of Connecticut, dated March 1999.

The ETPH Method measures the total of the C9 to C36 range of hydrocarbons, which includes the major components of a number of widely used petroleum products, as presented in Table 1. Because this method does not measure the lighter petroleum compounds, it is not suitable for the evaluation of gasoline, mineral spirits, petroleum naphthas, or other petroleum products that contain lower boiling components. In addition, the method is not suitable for higher boiling components (>C36) or distillates of aliphatic and/or aromatic hydrocarbons that are outside of the analytical range (C9 through C36 aliphatic and aromatic ranges) of the ETPH Method. While the ETPH Method is not suitable for measuring hydrocarbons <C9, it should be noted that the method **does** include volatile fractions of hydrocarbons (see Figure 1). Therefore, EPs should consider multiple lines of evidence to assess if ETPH concentrations may be indicative of a volatilization risk and if further evaluation of volatile petroleum hydrocarbons is warranted to be protective of human health and the environment.

3.1.1.1 *ETPH Reporting Limit*

Prior to the 2024 ETPH RCP (Version 3.0), an RL/LLOQ of 100 µg/L for aqueous samples was recommended. However, some laboratories reported difficulty in quantifying ETPH down to 100 µg/L due to instrument "noise" producing false positive results.

In response to feedback received from the laboratory community, an RL/LLOQ of 250 µg/L for aqueous samples was referenced in the *2012 Extractable Petroleum Hydrocarbon Fractions Using the ETPH Analytical Method and Criteria Development Technical Guidance Document*.

Based on the advances in laboratory practices since publication of the 2012 Technical Guidance Document, the current body of data indicates that an RL/LLOQ of 150 µg/L for aqueous samples is regularly achievable with high precision and accuracy. Therefore, the 2024 ETPH RCP references a "typical" RL/LLOQ of 150 µg/L for aqueous samples. However, laboratories should still be able to demonstrate the capability of quantifying at the lowest concentration possible above the instrument signal to noise level pursuant to RCSA 22a-134tt-1(d)(2). If a particular method cannot achieve desired RL/LLOQs then an alternative method may need to be utilized.

3.1.2 Extractable Petroleum Hydrocarbons

Petroleum products suitable for evaluation by the EPH method are identified in Table 1.

The EPH Method was developed and promulgated by the Massachusetts Department of Environmental Protection (MassDEP) in January 1998. The EPH Method is used to identify and quantify specific hydrocarbon ranges and target compounds that can be associated with certain petroleum products and/or found in petroleum releases. Identifying specific hydrocarbon ranges and/or target compounds can assist EPs with further development of the Site CSM and evaluate the potential risk of the release based on the CSM DQOs and regulatory criteria.

The EPH method identifies and quantifies (Table 3):

- Extractable aliphatic hydrocarbons within two specific ranges: C9 through C18, and C19 through C36;
- Extractable aromatic hydrocarbons within the C11 through C22 range; and
- Target PAH analytes

Table 3: EPH Analyte List

Range/ Target PAH Analyte	CAS No.
EPH Ranges	
C9 – C18 Aliphatic Hydrocarbons[1]	N/A
C19 – C36 Aliphatic Hydrocarbons[1]	N/A
C11 – C22 Aromatic Hydrocarbons[1,2]	N/A
Target PAH Analytes	
Naphthalene*	91-20-3
2-Methylnaphthalene*	91-57-6
Phenanthrene*	85-01-8
Acenaphthene*	83-32-9
Fluorene	86-73-7
Acenaphthylene	208-96-8
Anthracene	120-12-7
Fluoranthene	206-44-0
Pyrene	129-00-0
Benzo(a)anthracene	56-55-3
Chrysene	218-01-9

Range/ Target PAH Analyte	CAS No.
Benzo(b)fluoranthene	205-99-2
Benzo(k)fluoranthene	207-08-9
Benzo(a)pyrene	50-32-8
Indeno(1,2,3-cd)pyrene	193-39-5
Dibenz(a,h)anthracene	53-70-3
Benzo(g,h,i)perylene	191-24-2
[1] Hydrocarbon Range data exclude area counts of any surrogate(s) and/or internal standards eluting in that range. [2] C11-C22 Aromatic Hydrocarbons exclude the concentrations of Target PAH Analytes *Diesel PAH Analytes; these compounds must be analyzed when the presence of diesel is suspected.	

3.1.3 Volatile Petroleum Hydrocarbons

Petroleum products suitable for evaluation by the VPH Method are those identified in Table 1.

The VPH Method was developed and promulgated by the MassDEP in January 1998. Similar to the EPH Method, the VPH Method is used to identify and quantify specific hydrocarbon ranges and target compounds that can be associated with certain petroleum products and/or found in petroleum releases. Identifying specific hydrocarbon ranges and/or target compounds can assist EPs with further development of the Site CSM and evaluate the potential risk of the release based on the CSM DQOs and regulatory criteria.

The VPH Method identifies and quantifies:

- Volatile aliphatic hydrocarbons within two specific ranges: C5 through C8, and C9 through C12;
- Volatile aromatic hydrocarbons within the C9 to C10 range; and
- Target analytes identified in Table 4.

Table 4: VPH Analyte List

Range/ Target Analyte	CAS No.
VPH Ranges	
C_5 – C_8 Aliphatic Hydrocarbons[1,2]	NA
C_9 – C_{12} Aliphatic Hydrocarbons[1,3]	NA

Range/ Target Analyte	CAS No.
C_9 – C_{10} Aromatic Hydrocarbons	NA
Target Analytes	
Benzene	71-43-2
Ethylbenzene	100-41-4
Methyl-tert-butyl ether (MTBE)	1634-04-4
Naphthalene	91-20-3
Toluene	108-88-3
o-Xylene[5]	95-47-6
m-Xylene[4,5]	108-38-3
p-Xylene[4,5]	106-42-3
[1] Hydrocarbon Range data exclude area counts of any surrogate(s) and/or internal standards eluting in that range. [2] C5-C8 Aliphatic Hydrocarbons exclude the concentrations of Target VPH Analytes eluting in this range. [3] C9-C12 Aliphatic Hydrocarbons exclude the concentrations of Target VPH Analytes eluting in this range and the concentration of C9-C10 Aromatic Hydrocarbons. [4] May not be resolvable under chromatographic conditions required under this Method. [5] May be reported and evaluated as mixed isomers	

3.1.4 Air-Phase Petroleum Hydrocarbons

Petroleum products suitable for evaluation by the APH Method are those identified in Table 2.

The APH Method was developed and promulgated by the MassDEP in December 2009. The APH Method is used to identify and quantify gaseous-phase specific hydrocarbon ranges and target compounds that can be associated with certain petroleum products and/or found in indoor air and soil vapor associated with petroleum releases. Identifying specific hydrocarbon ranges and/or target compounds can assist EPs with further development of the Site CSM and evaluate the potential risk of the release based on the CSM DQOs and regulatory criteria.

The APH Method identifies and quantifies:

- Volatile aliphatic hydrocarbons within two specific ranges: C5 through C8, and C9 through C12
- Volatile aromatic hydrocarbons within the C9 to C10 range.
- Target APH analytes identified in Table 5.

Table 5: APH Analyte List

Range/ Target Analyte	CAS No.
Target Analyte	
1,3-Butadiene	106-99-0
Methyl-tert-butyl ether	1634-04-4
Benzene	71-43-2
Toluene	108-88-3
Ethylbenzene	100-41-4
m & p-Xylene[1]	1330-20-7
o-Xylene[1]	95-47-6
Naphthalene	91-20-3
APH Ranges	
C_5-C_8 Aliphatic Hydrocarbons[2,3]	NA
C_9-C_{12} Aliphatic Hydrocarbons[2,4]	NA
C_9-C_{10} Aromatic Hydrocarbons	NA
[1] May be reported and evaluated as mixed isomers [2] Hydrocarbon range data from total ion chromatogram excluding any internal/tuning standards eluting in that range. [3] C5-C8 Aliphatic Hydrocarbons exclude the concentrations of Target APH Analytes eluting in this range. [4] C9-C12 Aliphatic Hydrocarbons exclude the concentrations of Target APH Analytes eluting in this range and the concentration of C9-C10 Aromatic Hydrocarbons.	

3.1.5 Other Applicable Analytical Methods

The table below identifies analytical methods for compounds of interest and summarizes the method application. More details regarding the methods listed below can be found in their respective RCPs available on the Quality Assurance and Quality Control webpage and/or on the EPA website.

Table 6: Analytical Methods for Compounds of Interest[1]

Compound(s) of Interest	Method Number(s)[1]	Method Application
VOCs	SW-846 Method 8260	SW-846 Method 8260 is a purge and trap GC/MS method used to determine VOCs in a variety of matrices including waters, soils, sediments, wastes, etc. For petroleum releases, this method provides compound specific information which can be used to further develop the CSM.
SVOCs	SW-846 Method 8270	Method 8270 is a GC/MS method used to identify and quantitate SVOCs in a variety of matrices including waters, soils, sediments, wastes, etc. For petroleum releases, it provides concentration data for individual PAHs and other compounds.
PCBs	SW-846 Method 8082	Method 8082 is gas chromatography (GC) method used to evaluate concentrations of PCBs, as Aroclors or as individual congeners, in a variety of matrices including waters, soils, sediments, wastes, etc. This method is commonly used to assess waste oil, hydraulic oil and dielectric fluids (transformer oil) for PCBs. EPs may refer to the “Common Uses of PCBs” webpage on the DEEP website to further assess if PCBs are a contaminant of concern.

Compound(s) of Interest	Method Number(s)[1]	Method Application
Metals	SW-846 Method 6010 SW-846 Method 6020 SW-846 Methods 7000/7010 SW-846 Method 7196 SW-846 Methods 7470/7471	There are multiple analytical methods available for quantifying metals concentrations including SW 846 6010, 6020, 7000/7010, 7196, and 7470/7471 in a variety of matrices including waters, soils, sediments, wastes, etc. Each of these methods utilize instrumentation including inductively coupled plasma/optical emission spectrometry (ICP/OES), ICP/MS, Flame/Graphite Atomic Absorption, spectrophotometer, and Cold Vapor Atomic Absorption, respectively. For petroleum releases, they provide analyte specific information which can be used to further develop the CSM.
Vapor Phase Organics	TO-13 TO-15 TO-17[2] APH	There are multiple analytical methods available for quantifying organic contaminants in the vapor phase including TO-13, TO-15, TO-17, and APH (see section 3.1.4 of this document). When designing an analytical plan to identify and quantitate a release of petroleum products in soil vapor or indoor air, the EP should consider the substances which may be present based on the site history and select the appropriate analytical methods to identify and quantitate a release.
Drinking Water VOCs	EPA Method 524.2 EPA Method 524.3	GC/MS method used for analyzing VOCs in drinking water matrices.
Drinking water SVOCs	EPA Method 525.2 EPA Method 525.3	GC/MS method used for analyzing SVOCs in drinking water matrices.
Drinking water halogenated compounds	EPA Method 505 EPA Method 508.1	GC methods used for analyzing chlorinated pesticides, herbicides, and PCBs.

Compound(s) of Interest	Method Number(s)[1]	Method Application
Drinking water metals	EPA Method 200.7 EPA Method 200.8	Methods that utilize Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES/ICP-OES) and ICP Mass Spectrometry (ICP-MS), respectively, and are used for analyzing metals.

[1] More details regarding the methods listed below can be found on the following webpages:

- CT DEEP QA/QC Webpage: https://portal.ct.gov/DEEP/Remediation--Site-Clean-Up/Guidance/Quality-Assurance-and-Quality-Control#methods
- EPA Approved Drinking Water Methods: https://www.epa.gov/dwanalyticalmethods/approved-drinking-water-analytical-methods
- EPA Hazardous Waste Test Methods SW-846: https://www.epa.gov/hw-sw846

[2] Use of Method TO-17 analysis is appropriate for the screening of petroleum releases. Due to limitations of the sorbent material identified in Method TO-17, analytical data resulting from a TO-17 analysis is not considered representative when demonstrating compliance with the Release Based Cleanup Regulations (RBCRs).

4. FALSE POSITIVES FOR THE VPH, EPH, AND ETPH METHODS

EPs should be aware that due to the nature of the VPH, EPH, and ETPH analytical methods, detection, and quantification of ranges of organic compounds, there is potential for false positives of “petroleum” compounds. Since these analytical methods are non-discrete when analyzing and detecting carbon-based compounds, it is possible to detect other organic compounds such as VOCs (including chlorinated VOCs), SVOCs, organic matter (i.e., humic), PCBs, pesticides, and herbicides that are unrelated to petroleum products being characterized. It is the responsibility of EPs to fully characterize any release, using any necessary and applicable analytical methods, to identify and clarify any potential false positives to demonstrate the nature of the release.

False positives may occur when non-target compounds are detected concurrent with target compounds or within hydrocarbon ranges. False positives, confirmed by GC/MS analysis, may be reported in the laboratory report narrative by the laboratory. Experienced laboratory analysts can evaluate chromatograms for false positives; however, the experience of the analyst should weigh heavily on the interpretation of chromatograms.

Disregarding any analytical results as false positives must be supported by a scientifically valid explanation including chromatograms demonstrating confirmation of false positives by GC/MS analysis. Secondary lines of evidence such as the site history that are used to develop the CSM may be used to provide further evidence that a detection is a false positive, but such secondary lines of evidence aren’t sufficient by themselves to establish that a particular detection is a false positive.

4.1 Other Sources of Detected Petroleum Compounds

Materials commonly found on many sites in CT such as coal, coal ash, asphalt fragments, tar, and other asphalt products may result in petroleum detections. These materials are petroleum-based in nature, and the presence of these materials should not be equated with false positives in the analytical data; rather, further site investigation should be conducted to distinguish the possible sources.

5. REFERENCES

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- California State Water Resources Control Board, *Leaking Underground Fuel Tank Guidance Manual,* September 2012.
- Center for Environmental Research Information, Office of Research and Development U.S. Environmental Protection Agency, *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air Second Edition, Compendium Methods: TO-10A, TO-13A, TO-15, and TO-17*, January 1999.
- Connecticut Department of Energy and Environmental Protection, *Release Characterization Guidance*, effective March 1, 2026.
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- Connecticut Department of Environmental Protection, *Reasonable Confidence Protocols,* for various analytical methods. Revised 2024.
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- Massachusetts Department of Environmental Protection, Bureau of Waste Site Cleanup, *The Compendium of Quality Assurance and Quality Control Requirements and Performance Standards for Selected Analytical Methods Used in Support of Response Actions for the Massachusetts Contingency Plan (MCP).*
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- Total Petroleum Hydrocarbon Criteria Working Group Series, *Volume 2 Analysis of Petroleum Hydrocarbons in Environmental Media*, March 1998.
- United States Environmental Protection Agency, *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846)*, Update VII, and as may be amended from time to time.
- United States Environmental Protection Agency, *Method 418.1, Method 505, Method 508.1, Method 524.2, EPA Method 524.3, EPA Method 525.2, Method 8260, Method 8270, Method 8082.*