

CHARACTERIZATION OF C₆ TO C₃₅ PETROLEUM HYDROCARBONS IN ENVIRONMENTAL SAMPLES:

- TOTAL PETROLEUM HYDROCARBONS
- ALIPHATIC HYDROCARBONS
- AROMATIC HYDROCARBONS
- APPROXIMATE BOILING POINT/CARBON NUMBER DISTRIBUTION

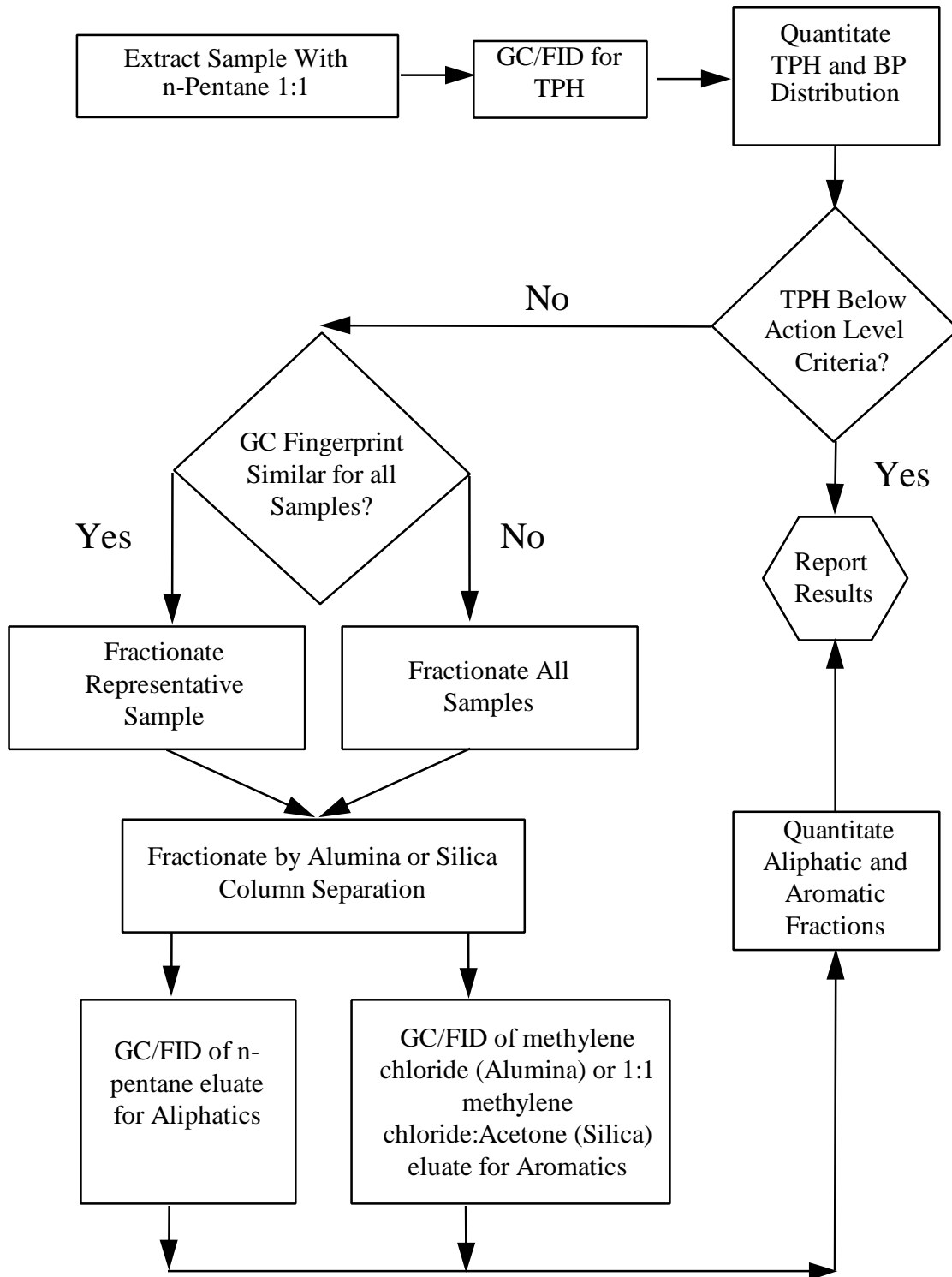
1.0 SCOPE AND APPLICATIONS

- 1.1 This gas chromatographic method is designed to determine the concentrations in soil and water of petroleum hydrocarbons from n-hexane (C₆) to n-pentatriacontane (C₃₅); an approximate boiling point range from 70⁰C to 500⁰C. This includes the gasoline, diesel range, and some portions of heavier fuels and lubricating oils. This method also describes the separation of the petroleum hydrocarbons into their aliphatic and aromatic fractions.
- 1.2 This method describes the characterization of the total petroleum hydrocarbons, the aliphatic, and the aromatic fractions into approximate carbon number/boiling ranges with respect to n-alkane markers. See Figure 1 for overall method options and when to apply them.
- 1.3 This method can be used to measure concentrations of individual target analytes. When target analyte information is desired, quantitation should be performed from the aliphatic or aromatic fractions rather than from the unfractionated extract. This will minimize the error due to coelution problems. However, target analytes are best determined using EPA Methods 8021, 8260 or 8270, where appropriate¹.
- 1.4 This method uses flame ionization (FID) as the mode of detection. The response of the FID is generally equal for all hydrocarbons on a weight and effective carbon number basis².
- 1.5 The method reporting limit is estimated to be 50 mg/kg in soil and 5 mg/L in water depending on the number of hydrocarbon components present in the C₆ to C₃₅ range. A limited interlaboratory evaluation of the method for total petroleum hydrocarbons in soil and in water has been conducted in Texas to validate TNRCC TX Method 1005³. In addition, a previous version of this method (using a split mode of injection) for total petroleum hydrocarbons in soil was subjected to an interlaboratory study conducted by The American Petroleum Institute⁴. It was found to have a PQL from 50 to 104 mg/kg (depending on the definition of PQL), an average accuracy of 84%, an average single analyst relative standard deviation (RSD) of 13%, and an average overall RSD of 30%. A similar study performed on this approach and the fractionation procedure by a single analyst showed an average accuracy of 80% with an average overall RSD of 6%. Also, an independent laboratory evaluation of this method resulted in a single analyst average accuracy of 111% and an overall RSD of 10%. Additional evaluation of this method has been done by the American Association of Railroads for applicability for diesel range materials⁵ and by A.D. Little, Inc. for applicability to crude oil

impacted soil. The latter effort studied the efficiency of n-pentane as an extraction solvent compared to methylene chloride and of vortex mixing versus Soxhlet. Both solvents and extraction mechanisms were found to be equivalent.

- 1.6 Petroleum and petroleum products with the majority of hydrocarbon components in the 70^oC to 500^oC boiling point range can be accurately extracted and measured by this method. This range includes gasoline, kerosene, diesel/fuel oil No.2, some lubricating oils and portions of other heavier oils.
- 1.7 This method should be used by, or under the supervision of, analysts experienced in the use of solvent extraction, solid phase fractionation and gas chromatography. The analysts should also be skilled in the interpretation of capillary gas chromatography data (specifically petroleum hydrocarbon pattern recognition), quantitation using computerized data acquisition, and use of peak processing software with baseline and peak grouping functions.
- 1.8 This method was originally developed to characterize petroleum hydrocarbons for proper remediation technology of impacted soils. Separation of the petroleum hydrocarbons into an aliphatic and an aromatic fraction was developed to provide data in the appropriate format to support the Total Petroleum Hydrocarbons Criteria Working Group (TPHCWG) risk-based corrective action approach to waste site remediation. This approach is based on the fate and transport and toxicological properties of petroleum hydrocarbon compound classes⁶.
- 1.9 The extraction and fractionation procedure can take as little as 15 minutes to perform per sample. GC analyses may take 20 to less than 90 minutes depending on the chromatographic column used and the GC parameters. Three separate GC analyses per sample are required to obtain total petroleum hydrocarbons, total aliphatics and total aromatic information. It is recommended that the sample extract be analyzed first to determine the type of petroleum hydrocarbons (if any) in the sample before proceeding with the fractionation step. Additionally, this information can be used for potential source identification, to assess if there are different types or distributions of petroleum hydrocarbons in a sample, or to determine if fractionation is necessary. If required, all or some of the sample extract may be fractionated into aliphatic and aromatic fractions which are then analyzed by GC.

Figure 1: Overall Method Options for Characterization of Petroleum Hydrocarbons



2.0 SUMMARY OF METHOD

- 2.1 This method involves extraction of a soil or a water sample with n-pentane and analysis of a portion of the extract using gas chromatography with a flame ionization detector (GC-FID). For additional characterization, fractionation of the petroleum hydrocarbon extract is accomplished by solid phase separation of another portion of the extract using alumina (similar to EPA Method 3611⁷) and eluting with n-pentane to obtain an aliphatic fraction followed by elution with dichloromethane to obtain an aromatic fraction. Alternatively, fractionation may also be done using silica gel (similar to EPA Method 3630C⁸). Silica gel may be more suitable for samples with a wide boiling point distribution of hydrocarbons. Silica gel may also be better for the fractionation of the higher molecular weight PNAs. In the silica gel procedure, a 1:1 mixture of acetone:methylene chloride is used to elute the aromatic compounds. Other fractionation procedures, such as automated HPLC methods, may also be used. The fractions are also analyzed using GC-FID. The extract as well as the fractions can be further characterized by subdividing the chromatographic data into approximate boiling point/carbon number ranges with respect to n-alkane markers.
- 2.2 This method allows choices of standards for calibration. Either mixtures of single hydrocarbon components, petroleum products (such as gasoline or diesel), or mixtures of petroleum products can be used. It is strongly encouraged that petroleum products similar to those present as contaminants in the samples be used if possible.
- 2.3 This method is based in part on USEPA Methods 8000, 8015, and 8100, SW-846, "Test Methods for Evaluation of Solid Waste", 3rd Edition¹. It is also similar to the Massachusetts Department of Environmental Protection Method for the Determination of Extractable Petroleum Hydrocarbons (EPH)⁹. This method is similar (for total petroleum hydrocarbons) to Washington State WTPH-HCID¹⁰. It was developed at Shell Development Company by I.A.L. Rhodes, L.P. Brzuzy, et.al.¹¹⁻¹³. This method was the basis for TNRCC TX Method 1005³.
- 2.4 This method uses n-pentane for the extraction of soil and water samples. Spiking studies done during method development and subsequent experiments at several laboratories with spiked and field samples show that n-pentane is equivalent to methylene chloride in extraction efficiency of hydrocarbons. The soil types ranged from sand to loam to clay. In addition, the vortexing extraction as well as Soxhlet extractions were found to be equivalent (unpublished PERF project results with crude oil in soil samples). Recent published work by the University of Toronto indicates that n-pentane is an excellent solvent for extraction of hydrocarbons from water¹⁴.

3.0 DEFINITIONS

- 3.1 **Total Petroleum Hydrocarbons (TPH)** are defined as all gas chromatographic peaks eluting after the solvent (n-pentane) starting with and including n-hexane(nC_6) to n-pentatriacontane (nC_{35}). This definition includes aliphatic and aromatic hydrocarbons. The petroleum hydrocarbons in a sample (if any) may not encompass the entire range. If the range of compounds present is narrower, then it is best to report on the observed range only. This information is useful for product or source identification. There may be non-hydrocarbon compounds that elute in this range (such as chlorinated solvents, ketones, alcohols, etc.). However, such compounds usually appear as discrete peaks and do not match typical petroleum product fingerprints. In some cases, such as when the samples contain crude or motor oil, only the portion within the nC_6 to nC_{35} will be measured as TPH.
- 3.2 **Aliphatic Hydrocarbons** are defined as those compounds detected from n-hexane (nC_6) to n-pentatriacontane (nC_{35}) (inclusive) in the chromatogram of the aliphatic fraction.
- 3.3 **Aromatic Hydrocarbons** are defined as those compounds detected from n-hexane (nC_6) to the retention time of n-pentatriacontane (nC_{35}) in the chromatogram of the aromatic fraction. The first aromatic compound is benzene.
- 3.4 **Approximate Boiling Point/Carbon Number Distribution** is defined as the subdivision of the chromatogram into sections that correspond to boiling point and/or volatility of n-alkanes. The gas chromatographic separation is achieved using a column that separates components based primarily on boiling point differences. This separation can be correlated to approximate carbon number. For example, $> C_7$ to $\leq C_8$ indicates those hydrocarbons that elute after n-heptane and up to and including n-octane. This range includes most, but not all, of the C_8 hydrocarbons. Branching lowers the boiling points of hydrocarbons relative to their n-alkane isomers. Cyclization, or ring structures, raises the boiling point higher than the n-alkanes of the same carbon number. Thus, there are some C_8 hydrocarbons that elute before n-heptane and there are some that elute after n-octane, including the aromatics ethylbenzene and the xylenes.
- This method allows for data reporting between each carbon range or for reporting within wider carbon ranges depending on data quality objectives. The TPHCWG has defined fractions based on different properties that effect the fate and transport and/or toxicity of petroleum hydrocarbon components.
- 3.5 **Aliphatic Hydrocarbon Standard** may be used to calibrate the analysis of the aliphatic or n-pentane fraction. The standard may be prepared from a mixture of n-alkanes and branched alkanes in n-pentane. This standard is not a requirement since it is recommended that a petroleum product or mixed products be used as standards for a single calibration that can be applied to extract and fractions.
- 3.6 **Aromatic Hydrocarbon Standard** may be used as an option to calibrate the analysis of the aromatic fraction. The standard can be prepared from a mixture of benzene, toluene, ethylbenzene,

xylenes, C3-benzenes (such as n-propylbenzene), C4-benzenes (such as t-butylbenzene), and polynuclear aromatics (such as the EPA target PNAs) prepared in dichloromethane. As indicated in 3.5, this standard is not required.

- 3.7 **Locator Mix Standard** will be used to determine the ranges C₆ to C₃₅ and the individual ranges specified in Table 2.
- 3.8 **An Analytical Batch** is defined as a set of 1 to 20 samples prepared on the same day.

4.0 INTERFERENCES

- 4.1 Other organic compounds, including vegetable and/or animal oils and greases, organic acids, chlorinated hydrocarbons, phenols, and phthalate esters are measurable under the conditions of this method. However, if present, the characteristic petroleum hydrocarbon patterns will be altered. These compounds will be quantified as part of the TPH, but the data should be flagged as presumptively containing significant amount of such compounds. The aliphatic and aromatic fractions may have less susceptibility to interferences from some types of materials because the fractionation process may remove the interference.
- 4.2 Sample contamination due to sample preparation may be minimized by the use of disposable glassware. A reagent blank should be analyzed with each set of 10 or less samples to demonstrate that the system is free from contamination. If samples are expected to have high concentrations, it is also advised that solvent blanks be analyzed between GC runs to minimize contamination due to carryover.
- 4.3 High purity reagent grade or pesticide grade n-pentane, dichloromethane and acetone should be used to minimize contamination problems.
- 4.4 This method depends on correctly integrating a mass of unresolved peaks using a forced baseline. The resulting baseline, if drawn incorrectly, will have a significant effect on the concentration reported. It is imperative that chromatograms be checked (using a realistic scale relative to the chromatogram) for correct baseline extension. Blanks and/or a low level standard should be run to monitor for baseline drift every 10 samples.

5.0 HEALTH AND SAFETY ISSUES

The toxicity of the reagents used in this method has not been precisely defined. However, each chemical compound should be treated as a potential health hazard. Exposure to these chemicals should be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file or material safety data sheets (MSDS) should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety should be available and should be identified for use by the analyst.

6.0 APPARATUS

6.1 Glassware

6.1.1 All specifications are suggestions only.

6.1.2 4 oz. (120 mL) amber glass wide-mouth jars.

6.1.3 Vials

6.1.3.1 10 to 40 mL glass vials with Teflon-lined screw caps.

6.1.3.2 2 mL GC autosampler vials with Teflon-lined crimp caps.

6.1.4 Disposable Pipets: Pasteur.

6.1.5 1 cm I.D. by 10 to 20 cm glass column with glass or Teflon stopcock.

6.1.6 Volumetric flasks and graduated cylinders

6.2 Microsyringes: 10 μ L to 1000 μ L.

6.3 Analytical balance capable of accurately weighing 0.0001 g should be used for preparation of standards. A top-loading balance capable of weighing to the nearest 0.01 g should be used for obtaining sample weights.

6.4 Vortex Mixer

6.5 Wrist action or horizontal shakers may be used for extraction.

6.6 Drying oven

6.7 Gas Chromatography

6.7.1 Gas Chromatograph: Analytical system which includes a splitless injector, column supplies, gases, and syringes. Electronic Pressure Control (EPC) is strongly recommended. A data system capable of storing and reintegrating chromatographic data and determining peak areas using a forced baseline and baseline projection is required. A gas chromatograph capable of performing baseline compensation is desirable

- 6.7.2 Recommended Columns
- 6.7.2.1 25/30 m x 0.25 to 0.53 mm ID fused silica capillary column with 0.25 to 1.5 μm film thickness (methyl silicone) or equivalent. Low bleed columns are preferred. Examples include MS-007 (Quadrex), DB-1 (J&W) and RTX-1 (Restek). DB-5 (J&W) may be used.
- 6.7.2.2 Other columns may be used if the elution of the compounds is based on boiling point. Capillary columns are recommended. See Section 9.3.2 for GC performance criteria.
- 6.7.3 Detector: A flame ionization detector (FID) is required.
- 6.7.4 Autosampler: An autosampler capable of making 1-4 μL sample injections is recommended

7.0 REAGENTS AND STANDARDS

- 7.1 n-Pentane, dichloromethane, acetone. Reagent grade, pesticide grade or equivalent.
- 7.2 Sodium Sulfate (ACS): Granular, anhydrous. Purify by heating at 100°C for 4 hours in a shallow tray.
- 7.3 Alumina, basic or neutral, Brockman activity 1, 150 mesh. Activate by heating at 350 °C at least 12 hours before using. Store at 110 °C until ready to use. Alternatively, Silica gel, 75-250 mesh. Activate at 110-130 °C until ready to use. In addition, solid phase extraction cartridges, or automated HPLC methods may be used but equivalency must be demonstrated.
- 7.4 **Calibration & Stock Standard Solutions:** This method allows for the choice of calibration standard for quantitation. The use of either a petroleum product(s) standard or a standard composed of selected hydrocarbons is acceptable. The selected hydrocarbon standard is required for the definition of carbon # retention windows and as a fractionation check solution. Unless noted, standards are prepared in the n-pentane listed in 7.1 above. Standard preparation should follow the guidelines outlined in EPA SW-846 Method 8000B.
- 7.4.1 **Petroleum Product Calibration Standard for Total Petroleum Hydrocarbons, Aliphatic and Aromatic Fractions:** The petroleum hydrocarbon calibration standard can be prepared by accurately weighing approximately 0.05 to 0.1 g (recorded to the nearest 0.0001 g) of a mixture of gasoline and diesel #2 in a 1:1 (either by volume or weight) ratio and diluting to volume with n-pentane in a 10 mL volumetric flask. If only the gasoline range or the diesel range TPH is of interest, then the calibration standards should be prepared with either 0.100 g gasoline or 0.100 g diesel. This 1% standard should be kept refrigerated. Typical working concentration ranges are between 5 to 5000 $\mu\text{g/mL}$. Calibration standards may be

prepared from a blend of selected hydrocarbons (as in Section 7.4.2).

7.4.2 Petroleum Hydrocarbon Calibration Standard, Approximate Boiling Point /Carbon Number Distribution Marker and Fractionation Check Stock Standard: This standard can be used for several purposes: for TPH calibration, for retention time window/approximate boiling point distribution marker (locator mix standard), and for alumina/silica gel fractionation performance check. The stock standard can be prepared by accurately weighing approximately 0.01 g (recorded to the nearest 0.0001 g) of each of n-alkanes [n-hexane (C₆) through n-eicosane(C₂₀) as well as n-pentacosane (C₂₅), n-octacosane (C₂₈) and n-pentatriacontane (C₃₅)] and diluting to volume with n-pentane in a 50 mL volumetric flask. It is also suggested that this standard contain 0.01 g each of benzene, toluene, ethyl benzene, o,m,p-xylene, cumene, as well as some or all of the target PNAs (naphthalene, anthracene, pyrene, etc.). Table 1 lists the boiling points of the n-alkanes. The laboratory should determine the retention times. The approximate concentration of this stock solution is 200 µg/mL per component. If this solution is to be used as a marker for retention time window/approximate boiling point distribution, accurate concentrations are not necessary. If the application requires that wider carbon ranges be used (ex: C₆ to C₁₀), this standard can be prepared with fewer n-alkane markers. This stock solution can be used for the determination of total petroleum hydrocarbons as well as the aliphatic and aromatic fractions if a component standard is preferred over a mixed product standard as described in 7.4.1 (please note limitations of this approach listed in 9.5.1). If available, a standard mix can be obtained from commercial suppliers.

7.4.3 Petroleum Products Reference Standards: To assist in the qualitative determination of product type or "fingerprint" of a possible petroleum product(s), it is recommended that a library of chromatograms be generated of gasoline, kerosene, diesel, motor oil, crude oils and any other pertinent product for comparison purposes. A recommended concentration range is 1000 to 5000 ppm. These may be obtained from several chromatography supply vendors.

8.0 SAMPLE COLLECTION, PRESERVATION, CONTAINERS, AND HOLDING TIMES

8.1 Soil samples are collected in wide-mouth glass jars with Teflon lined caps. Soils samples can also be collected and transported in core sampling devices¹⁵. Samples are stored at 4°C from the time of collection until extraction. Soil sample extraction and analysis should be performed within 14 days of collection. Depending on the analytes of interest and data quality objectives, other holding times may be applicable.

8.2 Water samples are to be collected by filling a 40 mL VOA vial with the sample and capping the vial with a Teflon septum cap (headspace free). Water samples may be preserved with HCl to a pH <2. Water sample analysis must be performed within 7 days of collection.

Table 1: Boiling points of n-alkanes used for the determination of approximate boiling point/carbon number distribution. Retention times based on GC conditions described in this method must be determined experimentally.

n-Alkane Marker	~Boiling Point, °C	n-Alkane Marker	~Boiling Point, °C
n-C6	69	n-C21	357
n-C7	98	n-C22	369
n-C8	126	n-C23	380
n-C9	151	n-C24	391
n-C10	174	n-C25	402
n-C11	196	n-C26	412
n-C12	216	n-C27	422
n-C13	236	n-C28	431
n-C14	253	n-C29	441
n-C15	270	n-C30	450
n-C16	287	n-C31	458
n-C17	302	n-C32	467
n-C18	316	n-C33	474
n-C19	329	n-C34	481
n-C20	343	n-C35	499

9.0 PROCEDURES

9.1 Sample Extraction

9.1.1 **Soil Extraction.** Extract soil samples using a vortex mixer or shaker technique.

9.1.1.1 Weigh 10 g of sample in a 40 mL vial with Teflon cap. Record the weight to the nearest 0.01 g. If needed, add enough sodium sulfate to make a loose-friable mixture (the use of sodium sulfate may not be necessary for dry soils). The sample should be free flowing prior to addition of the n-pentane. It is preferred that mixing of sodium sulfate with the sample be done as quickly as possible to minimize potential losses of volatiles. Add 10 mL of n-pentane, cap the vial and proceed with the extraction.

9.1.1.2 For a method blank, weigh 10 grams of Ottawa sand or other blank standard soil and extract as a sample.

9.1.1.3 For laboratory control samples (LCS) weigh 10 grams of Ottawa sand or other blank standard soil. For matrix spikes, weigh a separate 10 gram portion of sample. Add 0.25 mL to 1.0 mL

of stock solution to both the LCS and matrix spike as described in Section 7.4.1 and extract them like the samples.

- 9.1.1.4 Extract blanks, samples, LCS, matrix spike, and matrix spike duplicates by vortexing for at least 1 minute or shaking on a wrist action or horizontal shaker for at least 1 hour.
- 9.1.1.5 If particulate is suspended in the solvent layer or an emulsion forms, centrifugation may be necessary to obtain a clear solvent layer. Transfer a portion of the extract to autosampler vials for direct analysis of the extract for total petroleum hydrocarbons. The extract may be stored in vials with Teflon caps. Extracts should be stored at -15°C.
- 9.1.1.6 Anhydrous sodium sulfate may be used to aid in the drying and extraction of wet sediment or sludge samples. Weigh the sample into the vial then add up to 10 g of anhydrous sodium sulfate, cap and mix by vortexing. Add 10 mL of n-pentane, cap the vial and proceed with the extraction.9.1.1.7. If a sample of neat petroleum product, crude oil or waste is to be analyzed, the sample should be diluted in n-pentane (1:50 to 1:100) and analyzed directly. Alternatively, approximately 0.01g (~1 drop) of the material can be placed directly on the column for fractionation (Section 9.2).

9.1.2 Water Extraction. Extract water samples using a vortex mixer.

- 9.1.2.1 Remove sample in a 40 mL VOA vial from refrigeration and allow to come to ambient temperature. Remove approximately 10 ml of sample through the septum with a syringe. It is recommended that a needle be inserted into the septum at the same time to allow for flow of air into the vial as the 10 mL of water are removed. Dry the outside of the vial with a paper towel. Weigh the vial and its contents on a top loading balance and record the weight to the nearest 0.01 g.
- 9.1.2.2 Using a 5 mL glass syringe, add 3 mLs of n-pentane through the septum of the 40 mL VOA vial.
- 9.1.2.3 For laboratory method blanks, perform the procedure as in Section 9.1.2.1 using a VOA vial filled with approximately 30 mLs of reagent water.
- 9.1.2.4 For matrix spikes and laboratory control samples (LCS), perform the procedure as in Section

9.1.2.1, but add 0.1 mL of stock from Section 7.4.1 to 30 mL of a sample or distilled water prior to extraction.

- 9.1.2.5 Extract samples, LCS, blanks, matrix spikes, and matrix spike duplicates by vortexing for at least 1 minute.
- 9.1.2.6 Remove extract by pipette and store in Teflon capped vials at 4°C.
- 9.1.2.7 Discard the water from the VOA vial and dry the vial, lid, and septum in a drying oven at 70°C.
- 9.1.2.8 Reassemble the vial and weigh it on a top loading balance and record the weight to the nearest 0.01 g.
- 9.1.2.9 Determine the sample volume by subtracting the initial vial weight obtained in 9.1.2.1 from the dry vial weight obtained in 9.1.2.8.

9.2. **Extract fractionation.** Fractionate extract into aliphatic and aromatic components, if required, to obtain information in format suitable for the risk based correction approach proposed by the TPHCWG⁶.

- 9.2.1 Prepare the column by placing approximately 1 cm of moderately packed glass wool at the bottom of the column. Assemble the stopcock making sure that it turns smoothly.
- 9.2.2 Fill the column with about 10 mL of dichloromethane. Add approximately 4 grams of activated alumina to the column (or if silica gel is used, 2 grams of activated silica gel). Ensure that it is packed uniformly by gently tapping the side of the column. Top the column with approximately 0.5 cm of sodium sulfate. Then rinse the column with at least 10 additional mL of dichloromethane. Let the solvent flow through the column until the head of the liquid in the column is just above the top of the column (alumina packing nearly exposed). Discard the eluted dichloromethane. Add about 2 mL of n-pentane. Open the stopcock and let the solvent flow until the liquid in the column is just above the top of the column. Add 10-20 mL of n-pentane in the same manner just described. Open the stopcock and let the n-pentane flow until the head of the liquid is just above the top of the column. Discard the eluant. The column is ready for use.

Note: The performance of the alumina or the silica gel is dependent on the particular lot number of alumina or silica gel from the manufacturer, the humidity of the laboratory environment, and the activation temperature. Each laboratory may need to raise or lower the activation temperature depending on their particular conditions to achieve optimal separation.

- 9.2.3 Add 1 mL of the sample extract to the column. Open the stopcock and start collecting the eluant immediately in a 10 mL graduated cylinder, a 10 mL volumetric flask or any appropriate measuring vial. When the head of the n-pentane extract nearly reaches the top of the alumina or silica gel column, add n-pentane to the column in 1-2 mL increments while continuing to collect the eluant. It is best to add the solvent nearly dropwise with a pipette or wash bottle. Continue this approach until an accurately measured volume (8-10 mL) of the eluant is collected. Cap the vial and label this fraction "aliphatics".
- 9.2.4 Once the 8-10 mL of the n-pentane (aliphatic) fraction has been collected, proceed to collect in another graduated cylinder, volumetric flask or appropriate measuring vial the aromatic fraction by elution with dichloromethane. This is done in the same manner as in 9.2.3 by collection of the eluant immediately after addition of dichloromethane in 1-2 mL increments or dropwise. It is critical that the first 3-4 mL be added carefully and slowly. Once 8-10 mL have been collected, cap the vial and label this fraction "aromatics". If silica gel is used elute this fraction with a 1:1 mixture of acetone:methylene chloride.
- 9.2.5 Fractionation of neat petroleum products, crude oil and wastes is done by directly placing on the alumina or silica gel column 1 drop of the sample or by weighing approximately 0.01 g of the sample, adding 1 mL of n-pentane and then proceeding with the fractionation as defined in Section 9.2.3.

NOTE: It is critical that extreme care be taken on the elution of aliphatic and aromatic fractions to optimize the fractionation process. This optimization can be achieved by allowing the extract to elute from the column as much as possible before the addition of additional solvent: run the sample nearly out of the column before more solvent is added. Add additional solvent in small increments to the column to separate and obtain the fractions in narrow bands.

The amount of pentane and methylene chloride or acetone:methylene chloride used to elute the aliphatic and aromatic fractions, respectively can be optimized experimentally. Use enough pentane to elute all the saturates. This may require as little as 8 mL, but no more than 12 mL of pentane. Recoveries of aliphatics should be greater than 80%. If more the 12 mL of pentane is used, elution of aromatic compounds in the aliphatic fraction may result. For the aromatic fraction, use enough methylene chloride to ensure that all the aromatic compounds, especially the PNAs, have eluted from the column. Again, recoveries should be greater than 80%. Minimizing the amount of solvent used will increase the sensitivity of the analysis by avoiding overdilution of the sample.

- 9.2.6 Extract concentrations exceeding 10,000 µg/mL TPH may need to be diluted to avoid alumina column overloading. Silica gel

- capacity has not been determined, it is recommended that extraction concentrations not exceed 10,000 ug/mL.
- 9.2.7 The blank, LCS, matrix spike and matrix spike duplicate must also be fractionated with the sample batch.

9.3 Gas Chromatography

9.3.1 Gas Chromatographic Conditions

- 9.3.1.1 Oven Program: Set the initial column oven temperature to 10°C and hold for 1 to 5 minutes. Then ramp at 4 to 10°C/minute to 320°C and hold for 10 to 15 minutes. Alternatively, set initial column oven temperature to 30°C and hold for 3 to 4 minutes. Ramp at 10 to 20°C/minute to 300 to 320°C, hold for up to 10 minutes. Any oven program used must demonstrate adequate separation between the solvent and n-hexane (the first compound to be included in the TPH measurement).
- 9.3.1.2 Sample/autosampler injection: 1 to 4 µL splitless injection.
- 9.3.1.3 Carrier gas: Helium at 15 psig for a .25 mm ID column or as recommended by column manufacturer (lower pressures are required for larger IDs). If electronic pressure control (EPC) is used, the pressure will be variable.
- 9.3.1.4 Make-up gas: Nitrogen preferred (Helium can be used (30 mL/min))
- 9.3.1.5 FID hydrogen and air set to manufacturers' specifications
- 9.3.1.6 FID temperature: 325°C to 350°C
- 9.3.1.7 Injection port temperature: 300°C to 325°C
- 9.3.1.8 GC operated in splitless mode. Turn split on 1 minute after injection. Alternatively, a direct injection (Uniliner) technique may be used.
- 9.3.2 Performance Criteria: GC run conditions and columns should be chosen to produce chromatograms with adequate separation between the solvent front and n-hexane (the earliest eluting compound of interest that defines the beginning of the first carbon range) In addition, clear baseline resolution in the C₆ to C₁₂ range should be achieved

NOTE: Adequate separation of n-hexane from the solvent front (n-pentane) may be difficult with thin film columns

(<0.32 mm film thickness). The thin film columns facilitate the elution of hydrocarbons up to n-C₃₅ within a reasonable time. Thus, there may be some columns that may compromise the ability to analyze the entire C₆ to C₃₅ range adequately. The thicker film columns work quite well in the C₆ to C₂₈ range.

9.4 Retention Time Windows

- 9.4.1 Before establishing windows for integration using n-alkanes as markers, make sure that the GC system is within optimum operating conditions. Make three injections of the boiling point distribution standard defined in 7.4.2 throughout the course of a 72-hr period.
- 9.4.2 Calculate the standard deviation of the absolute retention times for each individual component in the boiling point distribution standard.
- 9.4.3 The width of the retention time window for each analyte is defined as plus or minus three standard deviations of the mean absolute retention time established during the 72-hour period. If a standard deviation of 0.00 is obtained, check reference SW-846 8000B Section 7.6.3 for further instructions¹. Analyst experience should be part of the interpretation of the chromatograms.
- 9.4.4 Alternatively, a default window may be chosen. This approach is preferred over the one described above because capillary columns are reliable with sufficient overall long term stability to maintain RT appropriately. This approach is also extremely simple. A window of \pm 0.1 minutes should be adequate.
- 9.4.5 The laboratory should reassess retention time windows for each standard on each GC column and whenever a new GC column is installed.
- 9.4.6 TPH retention time (RT) ranges are defined as beginning 0.1 minutes before the RT of the beginning marker compound (n-hexane) and ending 0.1 minutes after the RT of the ending marker compound (n-pentatriacontane or the last peak that elutes for a given sample if the last peak elute earlier than n-pentatriacontane). This RT range is applicable for the determination of TPH, aliphatic TPH, and aromatic TPH.
- 9.4.7 The approximate boiling point/carbon number distribution for the samples can be determined using n-alkane to define carbon # ranges of interest. The chromatograms obtained from analysis of TPH, aliphatic TPH and aromatic TPH can be subdivided into individual boiling ranges/approximate carbon numbers based on these RT windows. The TPHCWG has defined several aliphatic and aromatic fractions for the RBCA approach. These fractions encompass several carbon ranges which can be obtained the same way but using either addition of the individual carbon ranges or by defining wider carbon

ranges for measurements. The marker compounds are defined in Table 1.

- 9.4.8 TPHCWG Aliphatic and Aromatic Fractions: The TPHCWG has defined approximate carbon ranges of aliphatic and aromatic fractions based on fate and transport considerations. The fractions are listed in Table 2. This method can provide this information by either defining the RT ranges using the corresponding n-alkane markers for the characterization of the aliphatic and aromatic fractions with the exception of the aromatic fraction where practical quantitation stops at C₃₅.

9.5 Calibration

Calibrate the GC system using the external standard procedure

- 9.5.1 The method takes advantage of the fact that the response of the FID is essentially the same for all hydrocarbons (on a weight basis) and based primarily on effective carbon number². Any other compound containing heteroatoms will have some reduced response with respect to hydrocarbons because of lower carbon to hydrogen ratio. It is therefore not essential that calibration be performed using material similar to the material in the samples. For example, any gasoline, diesel, synthetic mixture, or single hydrocarbon can be used for calibration. However, because products such as gasoline or diesel are composed of more than 300 individual components, at low concentration of total product, many of the individual components are simply too small to be detected and cannot contribute to the total signal detected and thus linearity falls off. Conversely, when synthetic standards are used, typically no more than 10-20 components are used and thus the TPH is distributed among a few peaks that can be all detected for all concentrations of the standards above the stated practical quantitation limits. The use of synthetic standards can result in underestimation of the TPH present in the samples.

Table 2: TPHCWG Fate and Transport Fractions

Aliphatics	Aromatics
	>C5 to C7 (Benzene)
≥C6 to C8	>C7 to C8 (Toluene)
>C8 to C10	>C8 to C10
>C10 to C12	>C10 to C12
>C12 to C16	>C12 to C16
>C16 to C21	>C16 to C21
	>C21 to C35

- 9.5.2 External Standard Calibration Procedure: Guidance is provided for calibration and calculations using calibration factors. However, it is strongly recommended that a chromatographic data system be used for data

acquisition and processing. The baseline may rise as a result of column bleed at the higher temperatures towards the end of the run. Baseline compensation may help in integration of the chromatogram over the background from column bleed.

9.5.2.1 Prepare calibration standards from one of the stock solutions described in 7.4.1 or 7.4.2 at a minimum of five concentration levels by adding volumes of the pertinent stock standard solutions to volumetric flasks and diluting to volume with n-pentane or dichloromethane. The following calibration levels are recommended: 20, 50, 100, 200, 500, 1000 µg/mL. Calculate the total concentration of the 7.4.2 multicomponent stock standard for TPH calibration by adding all of the concentrations of the individual compound (Ex: 200 µg/mL per component, if 20 components, then TPH is 4,000 µg/mL) before diluting to prepare the calibration standards.

9.5.2.2 Inject each calibration standard using the same injection volume (1 to 4 µL injections) and technique that will be used to introduce the actual samples into the gas chromatogram. Tabulate peak area responses against the concentration injected using a force baseline projection. The results can be used to prepare a calibration curve for quantitation. Linear and quadratic calibration fits may be adequate for the calculation of sample results. Alternatively, the ratio of the response to the amount injected, defined as the calibration factor (CF), can be calculated for the standard at each concentration. If the percent relative standard deviation (%RSD) is less than or equal to 25% over the working range, the average response factor can be used in place of a calibration curve. If linear regression analysis is used for quantitation, the correlation coefficient (R) must be at least 0.995.

$$\text{Calibration Factor (CF)} = \frac{\text{Total area of calibration standard}}{\text{Concentration of calibration standard}(\mu\text{g/mL})}$$

Note: It is recommended that area response from calibration standards be acquired in the same manner as samples.

$$\%RSD = \frac{\text{Standard deviation of 5 CFs}}{\text{Mean of 5 CFs}} \times 100$$

9.5.2.3 The calibration factor obtained in Section 9.5.2.2 can be used to calculate TPH, aliphatic hydrocarbons and aromatic hydrocarbons. The

same calibration factor can be used to calculate the concentration of hydrocarbons present within the n-alkane markers used for defining the approximate boiling point/carbon number distribution. Alternatively, the boiling point distribution can be obtained from normalization of the entire chromatogram (nC₆ to nC₃₅) and determination of area percent within n-alkane markers. It is best to use a chromatographic data system to handle these calculations. A separate calibration file with the additional retention times should be established for the hydrocarbon ranges of interest to determine the approximate boiling point distribution and/or selected hydrocarbon ranges, both total and fractionated.

- 9.5.2.4 The working calibration factor or calibration curve should be verified on each working day by the injection of a mid-point calibration standard. If the concentration or response for these standards varies from the standard value or predicted response by more than $\pm 25\%$, a new calibration curve should be prepared. It is advisable to check instrument performance and reanalyze a low concentration standard as well to verify instrument performance and linearity.

$$\text{Relative Percent Difference} = \frac{R1 - R2}{R_{\text{avg}}} \times 100$$

Where: R1 = Standard value or average CF
R2 = Calculated value or CF
Ravg = (R1 + R2)/2

- 9.5.2.5 Calibration of Selected Target Analytes: Selected components (target compounds such as benzene, toluene, ethylbenzene, xylenes, PNAs, n-alkanes) can be measured individually if desired. Assuming an equivalent calibration factor, the calibration curve or calibration factor developed above can be used for target analytes. Coelutions of these target compounds in complex hydrocarbon mixtures can be expected. This is more significant for the PNAs because of the large number of isomers that are present as the carbon number increases. The results from these analyses can result in overestimation of these target compounds. If necessary, confirmation and more accurate quantitation may be obtained by using EPA Methods 8021, 8260, 8270¹.
- 9.5.2.6 Chromatographic Data System: The concentration of specific analytes or hydrocarbon ranges may also be calculated from a calibration curve by use of regression analysis.

9.6 Product Type Identification

- 9.6.1 Chromatographic peaks with characteristic fuel fingerprints eluting between the solvent front and C₁₀ indicate the presence of gasoline range. Peaks between C₁₀ and C₂₅ indicate the presence of diesel range compounds. Patterns that do not resemble either product should be noted.
- 9.6.2 Product type can be determined by visual inspection of the chromatograms. Chromatograms can become more complicated if crude oil, jet range material, or other refined products are also present. However, it may still be possible to determine that the contamination is due to some sort of petroleum product. Industrial solvents can interfere in the analysis; however, the chromatographic fingerprints would be noticeably different. The best approach to maximize the probability of a correct identification is to analyze reference fuels, from the sample location, along with the sample (if available). These reference fuels can also be used as calibration standards if desired.
- 9.6.3 As with any gas chromatographic procedure using non-selective flame ionization detection, interferences are possible from coelution of gasoline components with soil contaminants of other sources. Potentially, any compound with similar boiling point and polarity as the hydrocarbons of gasoline-to-diesel range may have retention times within the range of interest and may result in over-estimation of the TPH concentration. For example, volatile industrial solvents, cleaners, and naturally occurring compounds not of petroleum origin may interfere with this analysis. It is often possible to recognize the presence of solvents and cleaners since the characteristic fingerprint of gasoline, kerosene, diesel, and heavier materials is altered.
- 9.6.4 Decisions should be made by the analyst in determination of cutoff points for quantitation of different product ranges when contamination is caused by a combination of sources. For example, if soils are contaminated with gasoline range and diesel range materials, there is an area of overlap where certain components are common to both types of petroleum fractions. A compromise cutoff for mixtures of gasoline with diesel fuel range material is C₁₀. There is no appropriate cutoff for a mixture of jet fuel or kerosene since there is a great deal of overlap. Crude oil contamination also contains a wide range of materials. In cases where mixed products are present, it is perhaps best not to quantitate how much is due to what type of product but to simply quantitate total hydrocarbons and state the approximate carbon range observed.

In order to minimize quantitation problems due to column bleed, the method is best suited for analysis of materials up to diesel range. Heavier materials can be detected with a qualitative identification of product mix but not quantitated effectively.

9.6.5 Additional information on hydrocarbon pattern interpretation is included in some of the references cited¹¹⁻¹³.

9.7 **Gas Chromatographic Analysis**

9.7.1 Samples are analyzed by GC/FID. Suggested injection volumes are 1 to 4 µl using the conditions established in 9.3.

9.7.2 After initial calibration (9.5.2) has been performed, verify the calibration by analysis of a mid-point standard at the start of a new analytical sequence using the criteria in 9.5.2.4.

9.7.3 For samples that contain unresolved hydrocarbons, baseline projection should be used to generate the area for TPH calculation or for a group within a defined boiling range/carbon number. The GC conditions used for this method produce minimal column bleed up to C₃₅.

9.7.4 Alternatively, if peak resolution is adequate, valley-to-valley integration may be used to generate peak areas. This is only possible in the gasoline range (up to C₁₂) The analyst should avoid discarding chromatographic area related to unresolved hydrocarbons.

9.7.5 If the product concentration exceeds the linear range of the method in the final extract, the extract should be diluted and reanalyzed. The upper end of the linear range is defined as the highest standard in the calibration curve. The linear range tested is approximately equivalent to 50 µg/mL to 10000 µg/mL of petroleum hydrocarbons in the extract. Linearity beyond this range should be verified.

9.8 **Calculations**

9.8.1 External Standard Calibration: The concentration of TPH, aliphatic hydrocarbons, aromatic hydrocarbons, selected hydrocarbon ranges, or target analytes in a sample can be calculated from the appropriate area using either calibration factors or regression analysis.

$$C_s = \frac{C_c \times V_t \times D \times 1 \text{ mg}}{W_s \times 1000 \text{ } \mu\text{g}}$$

Where:

C_s = Concentration of TPH, hydrocarbon range or specific analytes (mg/kg or mg/L).

C_c = Concentration from calibration curve in µg/mL. (If CF is used for calculations, this value is area calibration/CF).

- Vt = Volume of extract (mL).
- D = Dilution factor, if dilution was performed on the sample prior to analysis. If no dilution was made, D = 1, dimensionless.
- Ws = Weight of sample extracted (kg). If a water sample, then the units are L.

9.8.2 The peak areas may be divided into desired carbon ranges/boiling point distribution if so desired. Patterns that do not resemble hydrocarbon products should be noted if the analyst is familiar with pattern recognition/fingerprints of petroleum products.

9.9 Calculation of Approximate Boiling Point Distribution: The approximate boiling point distribution is calculated by normalization of sums of peak areas of portions of the chromatograms eluting between preselected retention times as indicated in **Table 1**. Actual retention times should be verified in the laboratory. These retention times correspond to known boiling points selected as references. Characterization by individual approximate carbon number ranges is done up to C₃₅. This is only a guideline. Other markers or groupings can be used. The chromatographic column used in this method is primarily a boiling point, non-polar column. Compound separation is achieved by boiling point differences. A homologous series of n-alkanes is used to approximate boiling point references.

10.0 QUALITY CONTROL

10.1 General Requirements and Recommendations

- 10.1.1 The laboratory should establish the ability to generate acceptable accuracy and precision. This should include the analysis of QC check samples plus the calculation of average recovery and the standard deviation of the recovery as outlined in EPA Method 8000B, Section 8.0¹.
- 10.1.2 The laboratory should, on an ongoing basis, demonstrate through the analysis of quality control check standards that the operation of the measurement system is in control. This should include calibration verification every 10 samples, method blank, LCS, matrix spike and matrix spike duplicate every 20 samples.
- 10.1.3 After successful calibration (Section 9.5), analyze a reagent blank sample with every analytical batch or sequence. The blank should not have petroleum hydrocarbons above the practical quantitation limit. In addition, n-pentane or dichloromethane solvent blanks should be run after samples suspected of being highly contaminated to determine if sample carryover has occurred.
- 10.1.4 Each laboratory should generate control limits based on the average recovery +/- 3 standard deviations.

For the LCS, the laboratory must meet the minimum criteria of 60-140% recovery for the whole TPH.

- 10.1.5 If any of the criteria in 10.3 and 10.4 are not met, the problem should be corrected before samples are analyzed.
- 10.1.6 Field blanks, duplicates, and matrix spikes are recommended for specific sampling programs. Matrix spikes should use the spike levels specified for laboratory control samples.
- 10.1.7 Performance evaluation samples from an independent commercial source for both soil and water samples at both low (5-8 mg/L for water and 50-100mg/Kg for soil) and high (20-50 mg/L for water and 1,000-20,000 mg/Kg for soil) levels should be analyzed prior to performing analysis. Data and chromatograms for these PE samples must be kept on file at the laboratory for audit purposes. The performance evaluation samples should be analyzed yearly.

10.2 Minimum Instrument QC

- 10.2.1 The instrument should be able to achieve adequate separation and resolution of peaks and analytes of interest.
- 10.2.2 The n-hexane (nC₆) peak should be adequately resolved from the solvent in the chromatographic run.
- 10.2.3 Retention time windows should be established for each analyte and/or carbon range of interest each time a new GC column is installed, and should be verified and/or adjusted on a daily basis.
- 10.2.4 Calibration curves should be developed based upon the analysis of calibration standards prepared at a minimum of 5 concentration levels. The linearity of calibration or calibration factors may be assumed if the percent relative standard deviation (%RSD) over the working range of the curve is less than or equal to 25%. Alternatively, if linear regression analysis is used for quantitation, the correlation coefficient (r) should be at least 0.995.
- 10.2.5 In order to demonstrate the absence of mass discrimination, the response ratio of C35 to C20 should be at least 0.80.

10.3 Initial and Periodic Method QC Demonstrations

The following should be conducted as an initial demonstration of laboratory capability, prior to the analysis of any samples. Subsequent to this initial demonstration, additional evaluations of this nature should be conducted on a periodic basis, in response to changes in instrumentation or operations, and/or in response to confirmed or suspected systems, method, or operational problems.

10.3.1 Accuracy and Precision

To demonstrate initial laboratory capability, analyze a minimum of four replicate deionized water and clean sand blanks spiked with the TPH standards in Section 7.4.1 or 7.4.2 at approximately 10 to 20 mg/L (water) and 100 to 200 mg/kg (soil).

10.3.1.1 Extract and analyze each replicate according to the procedures described in Section 9.0.

10.3.1.2 Calculate the measured concentrations of TPH from nC₆ to nC₃₅ in all replicates, the mean accuracy (as a percentage of true value) for each analyte, and the precision (as %RSD) of the measurements for each analyte.

10.3.1.3 For each determination, the mean accuracy, expressed as a percentage of the true value, should be between 60% and 140%.

10.3.1.4 If desired, the accuracy and precision evaluation may be combined with the MDL evaluation specified in Paragraph 10.3.2.

10.3.2 Method Detection Limits

10.3.2.1 Soil/sediment MDLs are determined by extracting 7-10 replicates of 10 g of clean sand blanks which have been fortified with either of the stock solutions defined in Sections 7.4.1 or 7.4.2 at approximately 50 mg/kg. Extract and analyze each replicate according to the procedures described in Section 9.0. Calculate the Method Detection Limit (MDL) using guidelines in SW-846¹

10.3.2.2 Water MDLs are determined by extracting 7-10 replicates of deionized water fortified with stock solution in 7.4.1 or 7.4.2 at approximately 5 mg/L. Extract and analyze each replicate according to the procedure described in section 9.0. Calculate the Method Detection Limit (MDL) using guidelines in SW-846¹.

10.3.3 Fractionation

The stock solution described in Section 7.4.2 can be used to demonstrate the capability of properly fractionating aliphatic and aromatic hydrocarbons in a sample.

- 10.3.3.1 Prepare the column and follow the fractionation as described in Section 9.2 for the fractionation of 1 mL of the stock solution in Section 7.4.2.

Note: The amount of n-pentane used during fractionation is critical. Excessive n-pentane will cause elution of aromatics into the aliphatic fraction. Insufficient n-pentane will cause low recoveries of the aliphatic fraction. The volume of n-pentane recommended (8-10 mL) may need to be adjusted to meet QC limits.

- 10.3.3.2 For each analyte within the fractionation check solution, the mean accuracy, expressed as a percentage of the true value, should be between 60% and 140%.

- 10.3.3.3 It is acceptable to encounter a 10-20% crossover of the fractions. This means that it is within the acceptance criteria of this method to have 10-20% aliphatics in the aromatic fraction and 10-20% aromatics in the aliphatic fraction.

10.4 Ongoing Method QC Demonstrations

- 10.4.2 At a minimum, with every batch of 20 samples or less the lab should analyze the following:

10.4.2.1 **Calibration Check Standard** - A mid-range calibration standard, prepared from the same stock standard solution used to develop the calibration curve, should be analyzed prior to sample analysis to verify the calibration state of the instrument. For large analytical batches that contain more than 10 samples, the analysis of an additional mid-range calibration check standard is recommended after the analysis of the tenth sample. If the relative percent difference (RPD) of any analyte within a calibration check standard varies from the predicted response by more than 25%, a new calibration curve should be prepared for that analyte (see Section 9.5). Any sample analyzed after the last acceptable check standard must be reanalyzed.

10.4.2.2 **Laboratory Control Sample** - A soil LCS is prepared by fortifying 10 g of a clean sand blank with 0.25 mL to 1.0 mL of one of the standards described in Sections 7.4.1 and 7.4.2. for spiking solutions. A water LCS is prepared by fortifying 30 mL of deionized water with 0.1 mL of standard

described in Sections 7.4.1 and 7.4.2. The spike recovery should be between lab generated control chart limits. If there is insufficient data to control chart the maximum default limits of 60% to 140% may be used.

10.4.2.3 **Matrix Spike (MS) and Matrix Spike Duplicates (MSD)** - A soil matrix spike is prepared by fortifying an actual sample with 0.25 mL to 1.0 mL of the matrix spiking solution. A soil matrix spike duplicate is prepared the same way as the soil matrix spike. A water matrix spike is prepared by fortifying an actual sample with 0.1 mL of the matrix spiking solution. A water matrix spiked duplicate is prepared the same way as the water matrix spike. The purpose of the matrix spike is to determine whether the sample matrix contributes bias to the analytical results. The purpose of the matrix spike duplicate is to determine the precision of the analysis. The background concentrations of the analytes in the sample matrix should be determined in a separate aliquot and the measured values in the matrix corrected for background concentrations. The corrected concentrations of TPH for the MS spike should be within the lab generated control limits for them LCS. If there is insufficient data to control chart the maximum default limits of 60% to 140% may be used. If the MS is outside of the control limits then the batch it represents should be noted as having matrix interference. The LCS should be used to show the method is not contributing to spike loss. If the LCS falls outside the lab generated control limits then that batch needs to be reanalyzed until the LCS falls within the generated control limits. The RPD of the duplicate samples (MS and MSD) should not exceed 30%. If insufficient sample is available for a MS and MSD, then an LCS duplicate must be analyzed. The LCS duplicate recovery must fall within generated control limits. The RPD of the LCS and LCS duplicate must be less than or equal to 30%D

10.4.3 If any of the performance standards specified in Section 10.4 are not met, the problem should be corrected before further samples are analyzed. Any samples run between the last QC samples that meet the criteria and those that are fallen out should be

rerun. If this is not possible, that data should be reported as suspect.

11.0 DATA PRODUCTION AND REPORTING

11.1 Calibration

Using the external calibration procedure (Section 9.5), calibrate the GC as follows:

11.1.1 Calculate a collective Calibration Factor (CF), or linear or quadratic regression relationship for the sum of all the peaks that comprise either of the standards defined in Sections 7.4.1 or 7.4.2 for the C₆ to C₃₅ range or a narrower range if the sample contains a smaller carbon range and the option is taken to use a narrower boiling product as a standard. The CF or regression correlation should be done on the total area and the total mass of hydrocarbons in the standard within the specified carbon range.

11.1.2 The CF or regression correlation obtained in Section 11.1.1 can be used to calculate the petroleum hydrocarbon concentrations for smaller carbon ranges within the total TPH. These results provide the approximate boiling point distribution/carbon number range information. An easier and more convenient approach is to calculate the area percents of the individual sums of the peaks within the individual carbon markers ranges normalized with respect to the total area of the C₆ to C₃₅ (TPH area). Then use these percentages to calculate the amounts of petroleum hydrocarbons within those ranges.

11.2 Data Reporting Format

11.2.1 The following information and data should be reported:

11.2.1.1 The sample matrix (soil, sediment, sludge)

11.2.1.2 The date(s) the sample was collected, received by the laboratory, extracted and analyzed

11.2.1.3 Note in the report if there were any problems observed with the samples as received, such as the physical condition of the containers, the temperature of the samples, and the use of appropriate preservatives. No need to include this information if no problems observed.

11.2.1.4 Moisture content if desired (not required in this method)

- 11.2.1.5 The calculated concentrations of TPH C₆ to C₃₅ (or whatever carbon range the sample contains), the approximate boiling point/carbon number distribution for the TPH.
- 11.2.1.6 If sample extract is fractionated, the calculated concentrations of aliphatic and of aromatic hydrocarbons C₆ to C₃₅ (or whatever carbon range the sample contains), the approximate boiling point/carbon number distribution for the fractions
- 11.2.1.7 The method reporting limit for the TPH, aliphatic and aromatic hydrocarbons as well as for the narrower ranges.
- 11.2.1.8 Chromatograms and data tables

12.0 METHOD PERFORMANCE

- 12.1 The method has been applied to the analysis of neat crude oil, gasoline, JP-4, and diesel. In addition, the method has been used for the analysis of soil samples impacted with crude oil and with petroleum products with different degrees of weathering. Recoveries are typically 80% or better for most samples.
- 12.2 A previous version of this method for TPH and approximate boiling point/carbon number distribution was tested by 12 laboratories. Single operator precision, overall precision and method accuracy were determined and found to be 13%, 30% and 84%, respectively. A similar study performed on this approach and the fractionation procedure by a single analyst showed an average accuracy of 80% with an average overall RSD of 6%. Also, an independent laboratory evaluation of this method resulted in a single analyst average accuracy of 111% and an overall RSD of 10%.
- 12.3 Additional method refinement and evaluation is in progress.

13.0 POLLUTION PREVENTION

- 13.1 The solvent used in this method poses little threat to the environment when recycled and managed properly.
- 13.2 The quantity of chemicals purchased should be based on the expected usage during its shelf life. Standards should be prepared in volumes consistent with laboratory use to minimize the volume of expired standards to be disposed.

14.0 WASTE MANAGEMENT

- 14.1 It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particularly to comply with the hazardous waste identification

rules and land disposal restrictions, and to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is also required.

15.0 REFERENCES

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