New Jersey Department of Environmental Protection
Site Remediation Program

EXTRACTABLE PETROLEUM HYDROCARBONS METHODOLOGY (Version 1.1)

New Jersey Department of Environmental Protection
Office of Data Quality
Analytical Method

Title:
Analysis of Extractable Petroleum Hydrocarbon Compounds (EPH) in Aqueous and Soil/Sediment/Sludge Matrices

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1.0 SCOPE OF APPLICATION

1.1 Scope

This method utilizes a gas chromatograph (GC) fitted with a flame ionization detector (FID) to determine the collective concentrations of extractable aliphatic and aromatic petroleum hydrocarbons in water and soil/sediment matrices.

1.1.1 This method can be used for the quantitative analysis of environmental samples (water, soil, sediment, and sludge) for residues from commercial petroleum products such as crude oil, diesel fuel, waste oil, fuel oil Nos. 2-6, lubricating oil, processed oil and bunker fuel.

1.1.2 This method shall not be used for the quantitative analysis of gasoline, mineral spirits, petroleum naphtha and other petroleum products which contain a significant percentage of hydrocarbons lighter than C9 in water and soil/sediment/sludge matrices at contaminated sites.

1.2 Applicable Programs

Underground Storage Tanks (UST), New Jersey Spill Fund, Comprehensive Environmental Response Compensation and Liability Act (CERCLA), Industrial Site Recovery Act (ISRA), Sludge Residuals, and Resource Conservation and Recovery Act (RCRA).

1.3 Method Advantages

1.3.1 This method replaces the Total Petroleum Hydrocarbons (TPH) method based on Freon 113 extraction and analysis by infrared spectroscopy (i.e., Method 418.1).

1.3.2 The FID response produces extractable petroleum hydrocarbon (EPH) chromatograms that can be used to calculate concentrations of specified carbon ranges for both aliphatic and aromatic fractions.

1.3.3 This method provides results for specific carbon number ranges in both aliphatic and aromatic fractions of EPH thereby providing a more accurate assessment of potential health risk at environmental sites.

1.4 Method Limitations

1.4.1 Lower boiling hydrocarbons may co-elute with extraction solvents.

1.4.2 The EPH measured by this method is quantitatively restricted to the semi-volatile components as partial loss of volatiles (including those compounds lighter than C9) occurs during the extraction and/or concentration process.

1.4.3 The gas chromatographic conditions are not designed for samples containing EPH with carbon numbers greater than C44.

1.5 Applicable Matrices

1.5.1 Surface water, ground water, and wastewater.

1.5.2 Soil, sediments or high solids sludge (>50%).

2.0 SUMMARY OF METHOD

2.1 This quantitative EPH method is adopted from the "Method for the Determination of Extractable Petroleum Hydrocarbons (EPH)," Massachusetts Department of Environmental Protection (1); the "Method for the Determination of Extractable Petroleum Hydrocarbons (EPH) Fractions," Washington State Department of Ecology (2); the "Leaking Underground Fuel Tanks Field Manual" of the California State Water Resources Control Board (3); "Test Methods for Evaluating Solid Waste" USEPA Method 8015B (4); "Method for the Determination of Total Petroleum Range Organics," Florida Department of Environmental Protection (5); and "Quantitation of Semi-Volatile Petroleum Products in Water, Soil, Sediment and Sludge," New Jersey Department of Environmental Protection OQA-QAM-025-02/08 (6).

2.2 This method is adapted with modifications from ASTM Method D3328-82 and the US Coast Guard Oil Spill Identification Procedure for Total Petroleum (7, 8).

2.3 Petroleum residues are extracted from sample matrices with methylene chloride, dried over sodium sulfate, solvent exchanged to hexane and concentrated in a Kuderna-Danish apparatus. The extracts are separated into aliphatic and aromatic fractions using silica gel columns, either commercially available or lab prepared. Each of the aliphatic and aromatic fractions are re-concentrated and subsequently analyzed separately by capillary column GC/FID. Each of the resultant chromatograms of the aliphatic and aromatic fractions are used to quantitate four distinct carbon number ranges. Each carbon number range is defined using equivalent carbon (EC) numbers. The EC number is related to a compound's boiling point and retention time on a gas chromatography column normalized to the actual carbon numbers of n-alkanes. For example, the EC of acenaphthylene is 15.06 because its boiling point and GC retention time are halfway between those of n-tetradecane (a straight 14-carbon chain compound) and n-hexadecane (a straight 16-carbon chain compound). The EC numbers are used because they are more closely related to environmental mobility. The four EC number ranges for the aliphatic fractions are: EC9 to EC12, EC12 to EC16, EC16 to EC21 and EC21 to EC40. Similarly, the resultant chromatograms of the aromatic fractions are used to quantitate four distinct carbon number ranges. The four carbon number ranges for the aromatic fractions are: EC10 to EC12, EC12 to EC16, EC16 to EC21 and EC21 to EC36.

Surrogate compounds are added to all samples before extraction and their recoveries are monitored. Percent recoveries for the surrogates can be expected to be in the 50 - 90 % range. Fractionating surrogates are added to the hexane extract just prior to fractionation to monitor the efficiency of the fractionation process. Percent recoveries for the fractionating surrogates can be expected to be in the 40 - 95% range.

2.3.1 The EPH concentration is determined by integration of the FID chromatogram (see section 11.2). Average calibration factors or response factors using the aliphatic standard mixture are used to calculate the concentration <u>of each carbon range</u>. Average calibration factors or response factors using the aromatic standard mixture are used to calculate the concentration <u>of each carbon range</u>. Concentrations of each carbon range from both fractions are summed for a total EPH concentration.

2.3.2 The sensitivity of the method may be dependent on the level of interference rather than on instrumental limitations. The quantitation limit for each carbon range in soil is approximately 10 mg/kg and in water 100 ug/L.

2.3.3 Approximate Dynamic Range

2.3.3.1 <u>EPH</u>

Soil 80 -16000 mg/kg
Aqueous 0.8 - 160 mg/L

2.3.3.2 <u>Individual Carbon Ranges</u>

Soil 10 - 2000 mg/kg
Aqueous 0.10 - 20 mg/L

2.4 Compounds

2.4.1 Aliphatic Hydrocarbon Standard

Aliphatic Hydrocarbon (EC #)
n-Nonane (C9)
n-Decane (C10)
n-Dodecane (C12)
n-Tetradecane (C14)
n-Hexadecane (C16)
n-Octadecane (C18)
n-Eicosane (C20)
n-Heneicosane (C21)
n-Docosane (C22)
n-Tetracosane (C24)
n-Hexacosane (C26)
n-Octacosane (C28)
n-Triacontane (C30)
n-Dotriacontane (C32)
n-Tetratriacontane (C34)
n-Hexatriacontane (C36)
n-Octatriacontane (C38)
n-Tetracontane (C40)

2.4.2 Aromatic Hydrocarbon Standard

Aromatic Hydrocarbon (EC #)
Acenaphthene (C15.5)
Acenaphthylene (C15.06)
Anthracene (C19.43)
Benzo[a]anthracene (C26.37)
Benzo[a]pyrene (C31.34)
Benzo[b]fluoranthene (C30.14)
Benzo[g,h,i]perylene (C34.01)
Benzo[k]fluoranthene (C30.14)
Chrysene (C27.41)
Dibenz[a,h]anthracene (C30.36)
Fluoranthene (C21.85)
Fluorene (C16.55)
Indeno[1,2,3-cd]pyrene (C35.01)
2-Methylnaphthalene (C12.89)
Naphthalene (C11.7)
Phenanthrene (C19.36)
Pyrene (C20.8)
1,2,3-Trimethylbenzene (C10.1)

3.0 INTERFERENCES

3.1 Method interferences are reduced by washing all glassware and then rinsing with tap water, distilled water, methanol, and methylene chloride.

3.2 High purity reagents such as Burdick and Jackson GC[2] methylene chloride, Baker capillary grade methylene chloride or equivalent must be used to minimize interference problems.

3.3 Before processing any sample, the analyst shall demonstrate daily, through the analysis of a method blank, that the entire system is interference-free.

3.4 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interference will vary considerably from source to source (e.g., fatty acids, biogenic materials, oxidized biodegradation products), depending upon the nature and diversity of the site being sampled. The silica gel cleanup procedure, USEPA SW-846 Method 3630B, can be used to overcome many of these interferences but unique samples may require additional cleanup approaches such as SW-846 Methods 3610B, 3620B and 3660B to achieve the necessary analytical sensitivity.

3.5 Naturally occurring alkanes may be detected by this method and may interfere with product identification. Naturally occurring plant waxes include predominantly odd carbon number alkanes from n-C25 through n-C35, and exhibit a dominant odd/even chain length distribution.

4.0 SAFETY

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been defined precisely. Each chemical compound should be treated as a potential health hazard. Exposure to these chemicals must 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 of material safety data sheets (MSDS) should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified for use by the analyst (9, 10).

5.0 APPARATUS AND EQUIPMENT

5.1 Sampling Containers

5.1.1 Prior to use, wash bottles and cap liners with aqueous detergent solutions and rinse with tap water, distilled water, and methylene chloride. Allow the bottles and containers to air dry at room temperature, place in a 105^{o}C (minimum temperature) oven for one hour, then remove and allow them to cool in an area known to be free of organic analytes.

5.1.2 Screw cap bottle - 40 mL PTFE-faced silicone cap liners.

5.1.3 Narrow mouth bottles - 1 liter, amber, PTFE faced silicone cap liners.

5.1.4 Wide-mouth glass jar-four ounce, amber, PTFE faced silicone cap liners.

5.2 Glassware

5.2.1 Serum bottles - 100 mL, 10 mL, 2 mL crimp-top, PTFE-faced silicone cap liners.

5.2.2 Pasteur pipettes.

5.2.3 Screw-cap Erlenmeyer flasks - 250 mL, with PTFE faced silicone cap liners.

5.2.4 Volumetric flasks - 10 mL, 25 mL, 100 mL.

5.2.5 Kuderna-Danish apparatus (KD), 500 mL flask.

5.2.6 Separatory funnels - 2 L Pyrex, Teflon stopcock.

5.2.7 Soxhlet Extractor with 500 mL flask.

5.2.8 1 cm I.D. by 10 to 20 cm long glass column with glass or Teflon stopcock.

5.3 Apparatus

5.3.1 Analytical balance capable of accurately weighing 0.0001 g.

5.3.2 A gas chromatograph with split/splitless injector, equipped with a capillary column, capable of temperature programming. The analytical column chosen must adequately resolve the n-C9 to n-C40 aliphatic standard compounds and the aromatic standard compounds listed in 6.8.1 and 6.8.2 below. The recommended column is:

5.3.2.1 Column - 30m long x 0.32mm I.D., 0.25um film thickness, 95% dimethyl-5% diphenyl polysiloxane (Restek RTX-5 or equivalent).

Recommended Conditions:
Oven Temperature: 60^{o}C; hold for 1 minute; 8^{o}/minute to 290^{o}C, hold for 7 minutes
Injection size: 1 - 4 uL
Gas Flow Rates: Carrier Gas - Helium @ 2 -3 mL/minute;
Oxidizer - Air @ 400 mL/minute;
Fuel - Hydrogen @ 35 mL/minute;
Make up - Air @ 30 mL/minute.
Injection Port Temperature: 285^{o}C
Column Inlet Pressure 15 p.s.i.
Detector Temperature: FID @ 315^{o}C
Linear Velocity: 50 cm/sec

5.3.2.2 Detector - Flame Ionization Detector is required.

5.3.3 An autosampler is recommended.

5.3.4 Boiling chips (Teflon® preferred) - Solvent extracted approximately 10/40 mesh.

5.3.5 Water bath - Top, with concentric ring cover, capable of temperature control. The bath should be used in a hood.

5.3.6 Gas-tight syringe - One milliliter (mL) with chromatographic needles.

5.3.7 Microsyringes - l0uL, 100uL, 200uL.

5.3.8 Magnetic stirrer and 2-inch Teflon coated stirring bars.

5.3.9 Nitrogen concentration system composed of a precleaned pasteur pipette, with a small plug of glass wool (previously washed with solvent and dried) loaded at the tip end, and filled with approximately 1-2 cm of precleaned alumina. The top of the pipette is attached to a hydrocarbon free nitrogen gas source using precleaned Teflon tubing. This concentration step should be performed at room temperature or lower to retain light end compounds.

6.0 REAGENTS

6.1 Purity of Reagents - Reagents are to be of the highest quality appropriate and shall conform to all pertinent specifications of the American Chemical Society.

6.2 Reagent water - Reagent water is defined as a water in which an interference is not observed at the MDL of each parameter of interest (ASTM Specification D1193, Type ii).

6.3 Methylene chloride, methanol, carbon disulfide and hexane - pesticide grade, Burdick and Jackson GC[2], Baker Capillary Grade or equivalent.

6.4 Sodium sulfate - (ACS) granular, anhydrous. Purify by heating at 400^{o}C for four hours in a shallow tray, cool in a desiccator and store in a sealed glass bottle.

6.5 Silica gel desiccant (for fractionation) - 100/200 mesh (Davison Chemical Grade 923 or equivalent). Before use, activate for at least 16 hours at 130^{o}C in a shallow glass tray that is loosely covered in foil. Cool and store as in section 6.4. Commercially available Solid Phase Extraction (SPE) cartridges (20 ml tube volume/5 g bed weight) may be used (Restek - Massachusetts TPH Specialty SPE Cartridge or equivalent). (Please note: Silica gel is hygroscopic. Unused cartridges must be stored in properly maintained desiccators prior to use to prevent absorption of moisture from air.)

6.6 Ottawa and/or masonry sand, free from extractable petroleum products, may be used in lieu of sodium sulfate for sections 9.2, 9.3 and 9.4.

6.7 Hydrochloric acid, 1:1 - Mix equal volumes of (ACS grade) concentrated HCl and distilled water.

6.8 Standard Solutions

6.8.1 Aliphatic Hydrocarbon Stock Standard - Prepare a hexane solution containing at a minimum the aliphatic compounds listed in Section 2.4.1, naphthalene, 2-methylnaphthalene and the surrogate (1-chlorooctadecane) each at a concentration of 1 mg/ml. (Naphthalene and 2-methylnaphthalene are added to the aliphatic standard as their presence in the laboratory control sample and/or laboratory control sample duplicate is used to determine if fractionation for a batch is acceptable.) Aliphatic mixtures are available from Supelco, Restek (Cat. # 31266), NSI Solutions and Ultrex. (Note: Due to the commercial availability of standards, it may be necessary to combine two commercially available standard mixtures which may result in the addition of compounds such as n-Nonane (C9) and n-Nonadecane (C19) to the aliphatic hydrocarbon standard.)

6.8.2 Aromatic Hydrocarbon Stock Standard - Prepare a methylene chloride solution containing the aromatic compounds listed in Section 2.4.2, the surrogate compound (ortho-terphenyl) and the fractionating surrogate compounds (2-Bromonaphthalene and 2-Fluorobiphenyl) each at a concentration of 1 mg/ml. (Aromatic mixtures are available from Supelco, Restek (Cat. # 31469), NSI Solutions and Ultrex.)

6.8.3 Surrogate - The surrogate ortho-terphenyl (OTP) is prepared by weighing 0.0100 g of pure material in a 10 mL volumetric flask. Dissolve the material to volume in methylene chloride. The surrogate 1-chlorooctadecane (COD) is prepared by carefully weighing 0.0100 g of pure material in a 10 mL volumetric

flask. Dissolve the material to volume with hexane. (Surrogate solutions are available from Restek Inc. [11].)

6.8.4 Surrogate Spiking Solution - Prepare a surrogate spiking solution containing OTP and COD at a concentration of 100 ng/uL each in acetone. Each sample, blank, and matrix spike is fortified with 1.0 ml of the surrogate spiking solution. Alternative concentrations are permissible and, in instances when spiking highly contaminated samples, the use of higher concentrations is advisable.

6.8.5 Laboratory Control Sample (LCS) (Blank Spike) Solution - The LCS solution is the same as the matrix spiking solution described in 6.8.6 below. 1 mL is used to fortify either reagent water or clean sand (or sodium sulfate).

6.8.6 Matrix spiking solution (MSS) - Prepare the MSS containing all the compounds in sections 2.4.1 and 2.4.2 in methanol or acetone each at a concentration of 100 ng/uL. The source of the standards shall be different than those from which the calibration standards are made. A 1 mL aliquot is added to the sample designated as the matrix spike. Alternative concentrations are permissible and, in instances when spiking highly contaminated samples, the use of higher concentrations is advisable.

6.8.7 Fractionating Surrogates: The fractionating surrogates (2-Bromonaphthalene and 2-Fluorobiphenyl) are prepared by weighing 0.0100 g of pure material in a 10-ml volumetric flask and dissolving the material in Methylene Chloride. (Surrogates are available from Restek Inc.)

6.8.8 Fractionating Surrogate Spiking Solution - Prepare the solution containing 2-Bromonaphthalene and 2-Fluorobiphenyl at concentrations of 100 ng/ul each in hexane. An aliquot of 1 ml of the fractionating surrogate spiking solution is added to the 1 ml EPH sample extract prepared in accordance with sections 10.1 and 10.2 just prior to fraction separation with silica gel. Alternative concentrations are permissible and, in instances when spiking highly contaminated samples, the use of higher concentrations is advisable.

6.8.9 Fractionating Check Solution - This solution is used to monitor the fractionation efficiency of the silica gel cartridge/column and establish the optimum hexane volume required to efficiently elute the aliphatic fraction without significant aromatic breakthrough.

Prepare the solution containing 200 ng/uL of all the compounds listed in the aliphatic hydrocarbon standard and 200 ng/uL of all the compounds listed in the aromatic hydrocarbon standard cited in sections 6.8.1 and 6.8.2 respectively, in hexane.

7.0 SAMPLE COLLECTION, PRESERVATION AND STORAGE

7.1 Aqueous Matrix

7.1.1 Collect a representative water sample in a 1 L narrow mouth bottle. A delay between sampling and analysis of greater than four hours requires sample preservation by the addition of 5 ml HCl (see section 6.7). Confirmation of a pH < 2 must be obtained in the field.

7.1.2 Sample must be chilled to 4±2^{o}C at the time of collection and stored at 4±2^{o}C until received at the laboratory.

7.1.3 The laboratory must determine the pH of all water samples as soon as possible after sample receipt and prior to extraction. Any sample found to contain a pH $>$ 2 must be noted in a laboratory notebook and the pH must be adjusted as soon as possible. Samples are to be stored at 4±2^{o}C until extraction.

7.1.4 Samples must be extracted within fourteen days from the time of collection. Extracts must be analyzed within 40 days of extraction.

7.2 Solid Matrix

7.2.1 Collect a representative soil-sediment sample in a four-ounce, wide-mouth jar with a minimum of air space.

7.2.2 Samples must be chilled at 4±2^{o}C at the time of collection and stored at 4±2^{o}C until analyzed.

7.2.3 Samples must be extracted within fourteen days from the time of collection. Extracts must be analyzed within 40 days of extraction.

8.0 CALIBRATION

8.1 Initial Calibration

8.1.1 Retention time windows

8.1.1.1 Before establishing windows, make sure the GC system is within optimum operating conditions. Make three injections of the Aromatic Hydrocarbon and Aliphatic Hydrocarbon standard mixtures. Serial injections over less than a 72 hr period result in retention time windows that are too restrictive.

8.1.1.2 Calculate the mean and the standard deviation of the three retention times (use any function of retention time including absolute retention time or relative retention time) for each individual compound in the aromatic standard, each individual compound in the aliphatic standard and all surrogates.

8.1.1.3 Plus or minus three times the standard deviation of the mean retention times for each compound in the aromatic and aliphatic standards will be used to define the retention time window; however, the experience of the analyst should weigh heavily in the interpretation of chromatograms. The default value for the retention time shall be a minimum of ± 0.1 minutes, if the standard deviation is zero or close to zero.

8.1.1.4 Establish the midpoint of the retention time window for each surrogate by using the absolute retention for each surrogate from the mid-concentration standard of the initial calibration. The absolute retention time window equals the midpoint + 3 SD, where the standard deviation is determined as described in section 8.1.1.2.

8.1.1.5 The laboratory must calculate retention time windows for each aromatic standard compound, each aliphatic standard compound and each surrogate on each GC column and whenever a new GC column is installed. The data must be retained by the laboratory.

8.1.2 FID External Standard Calibration for Quantitation of EPH. Calibrate the GC-FID with an initial five-point calibration. The recommended standard concentrations of each individual component are 20 ng/uL, 100 ng/ul, 250 ng/uL, 500 ng/uL and 1000 ng/uL. Separate calibrations are to be conducted for each fraction (see sections 6.8.1 and 6.8.2). The highest concentration point should be twice the expected sample concentration and within the linear range of the instrument. To maintain the standards in solution, a 10% carbon disulfide / 90% methylene chloride solvent may be required. Standards with concentrations greater than 20 mg/L may need to be equilibrated to room temperature prior to analysis. Prepare the calibration standards to contain 100 ng/uL of each surrogate. The surrogate OTP and the fractionating surrogates are included in the Aromatic Hydrocarbon Standard. The surrogate COD is included in the Aliphatic Hydrocarbon Standard.

A calibration factor (CF) must be established for each individual component. Also, a separate calibration factor (CF) must be established for each carbon range of interest. Calculate CFs for the C9-C12, C12-C16, C16-C-21 and C21-C40 Aliphatic Hydrocarbon carbon ranges from the appropriate aliphatic analysis chromatogram. Calculate CFs for C10-C12, C12-C16, C16-C-21 and C21-C36 Aromatic Hydrocarbon carbon ranges from the appropriate aromatic analysis chromatogram.

For the aliphatic fraction, use the following compounds as carbon range markers:

Range	Compound	EC
C9-C12	n-Nonane	9.0
	n-Dodecane	12.0
C12-C16	n-Dodecane + 0.1 min	
	n-Hexadecane	16.0
C16-C21	n-Hexadecane + 0.1 min	
	n-Heneicosane	21.0
C21-C40	n-Heneicosane + 0.1min	
	n-Tetracontane	40.0

For the aromatic fraction, use the following compounds as carbon range markers:

Range	Compound	EC
C10-C12	1,2,3-Trimethylbenzene	10.1
	Naphthalene	11.7
C12-C16	Naphthalene + 0.1 min	
	Acenaphthene	15.5
C16-C21	Acenaphthene + 0.1 min	
	Pyrene	20.8
C21-C36	Pyrene + 0.1min	
	Benzo(g,h,i)perylene + 1.0 minute	34.01

(Please note: The "+ 0.1 minutes" noted above in both the aromatic and aliphatic fractions are maximums. The laboratory should use less than the

"compound + 0.1 minute" as the carbon range marker if peak shape and chromatographic resolution are favorable.)

The Calibration Factor (CF) is defined as the ratio of the peak area to the concentration injected.

For individual compounds, the calibration factors are determined by the following equation.

$$CF = \frac{Area\ of\ Peak}{Concentration\ Injected\ (ng/uL)}$$

For the carbon ranges, tabulate the summation of the peak areas of all the compounds in each carbon range against the total concentration injected for that carbon range. The Calibration Factor (CF), defined as the ratio of the summed peak area to the concentration injected, is calculated for each carbon range using the following equation:

$$Carbon\ Range\ CF = \frac{Summed\ Area\ of\ Peaks\ in\ the\ Range}{Total\ Concentration\ Injected\ (ng/uL)}$$

Note that the areas for the surrogates must be subtracted out from the area summation of the range in which they elute. Also, any areas associated with naphthalene and 2-methylnaphthalene in the aliphatic fraction must be subtracted out from the appropriate carbon range.

The percent relative standard deviation (%RSD) of the calibration factors for each compound and surrogate must be ≤ 25% over the working calibration range.

$$\%RSD = \frac{Standard\ Deviation\ of\ 5\ CFs}{Mean\ of\ 5\ CFs}$$

The percent relative standard deviation (%RSD) of the calibration factors for each carbon range for the compounds and surrogates must be ≤ 25% over the working calibration range.

$$\%RSD = \frac{Standard\ Deviation\ of\ 5\ Range\ CFs}{Mean\ of\ 5\ Range\ CFs}$$

If any %RSD is >25%, the source of the problem should be identified and the problem resolved.

8.2 Daily Calibration

8.2.1 At a minimum, the working calibration factors for each fractional carbon range must be verified on each working day, after every 20 samples or every 24 hours (whichever is more frequent) and at the end of the analytical sequence by the injection of the mid-level calibration standards (both aliphatic and aromatic). Calculate the percent differences (D %) between the continuing calibration factors and the average calibration factors from the initial calibrations for each compound, for each carbon range for each fraction and for

the surrogates. If the %D of any carbon range is >25% (>30% for any single compound in a range) then a new calibration curve has to be generated for that range. Any sample associated with a non-compliant calibration shall be reanalyzed.

$$\%D = \frac{CF_{AVG} - CF_{cc}}{CF_{AVG}}$$

Where:

CF_{AVG} = Average Calibration Factor calculated from initial calibration
CF_{CC} = Calibration Factor calculated from continuing calibration standard

8.2.2 The retention times of surrogates in the calibration verification standard analyzed at the beginning of the analytical shift must fall within the absolute retention time windows calculated in Sec. 8.1.1.2. The purpose of this check is to ensure that retention times do not continually drift further from those used to establish the widths of the retention time windows. If the retention time of any surrogate at the beginning of the analytical shift does not fall within the ± 3 SD window (minimum ±0.10 min.), then a new initial calibration is necessary.

In addition, the retention times of all surrogates in the subsequent calibration verification standards analyzed during the analytical shift must fall within the absolute retention time windows established in Sec. 8.1.1.4.

8.2.3 Surrogate Standards (SS) - The SS responses and retention times in the calibration check standard must be evaluated during or immediately after data acquisition. If the retention time(s) for the SS is outside the determined RT window, the chromatographic system must be inspected for malfunctions and corrections must be made. If the area(s) for the SS changes by ±50% from the last daily calibration standard check, the GC must be inspected for malfunctions and corrections must be made.

8.3 Mass Discrimination Check

8.3.1 Mass discrimination can take place in the injection port of the gas chromatograph. The higher boiling point molecules may not enter the column with the same efficiency as the lower boiling point molecules with a resulting bias toward the lower boiling molecules. This phenomenon must be checked and if present corrected prior to calibrating and analyzing samples.

8.3.2 Mass discrimination is minimized by placing a small plug of silanized glass wool one centimeter from the base of the glass injection liner. The end of the capillary column is placed just below the glass wool. The capillary column should be placed flush with the surface of the gold seal. A full range alkane standard should be run to test the degree of mass discrimination before performing any actual sample analyses. The response ratio of C30/C20 shall be ≥ 0.8. If less than 0.8, the column should be repositioned until the mass discrimination is minimized.

9.0 QUALITY CONTROL

9.1 Each laboratory that uses this method is required to operate a formal quality control program which conforms to New Jersey Regulation N.J.A.C. 7:18-4.7 (12). The minimum requirements of this program consist of an initial demonstration of laboratory capability

and an ongoing analysis of QC samples to evaluate and document data quality. The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with laboratory established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

9.1.1 The analyst must make an initial, one-time demonstration of the ability to generate acceptable accuracy and precision with this method (see section 9.2).

9.1.2 In recognition of advances that are occurring in chromatography, the analyst is permitted to improve the separations by changing the GC conditions or column. Each time such a modification is made to the method, the analyst is required to repeat and document the procedure in section 9.2.

9.1.3 Each day before calibration and after the calibration, the analyst shall analyze a reagent blank (instrument blank) to demonstrate that interferences from the analytical system are under control. Peaks should not be detected above the quantitation limit within the retention time window of any carbon range of interest. If so, re-extraction of all associated samples may be warranted.

9.1.4 With each sample batch, the analyst must analyze a method blank to demonstrate that interferences from sample extraction are under control. Target compounds' concentrations in the blank should be no more than 5X MDL. If blank levels for any component are above 5X MDL and the sample concentrations present in the samples are greater than 10X then the samples may be quantified and qualified. If the blank concentration is greater than 5X MDL and the sample concentrations present in the samples are less than 10X the blank level, the affected samples should be re-extracted and re-analyzed. If a sample cannot be re-extracted or re-analyzed, the data must be qualified as such.

9.1.5 Contamination by carryover may occur when high concentration samples are analyzed. When highly contaminated sample extracts are analyzed, it is recommended that a solvent blank be analyzed immediately following to check for cross contamination. If contamination is present, the system must be cleaned before continuing sample analysis. If a sample immediately analyzed after the highly contaminated sample is free from contamination then it is safe to make the assumption that carryover or cross contamination is not an issue. However, if the sample(s) analyzed after the highly contaminated sample exhibits the same compounds and/or same chromatographic fingerprint and no system cleaning was implemented, then carryover or cross-contamination may be suspected and all affected samples may be required to be reanalyzed.

9.1.6 The laboratory must, on an ongoing basis, demonstrate through the analyses of a Laboratory Control Sample (LCS) and Laboratory Control Sample Duplicate (LCSD) that the operation of the measurement system is in control. This procedure is described in sections 9.3 and 9.4. The frequency of the LCS/LCSD pair is one in every 20 samples of similar matrix.

9.1.7 The laboratory must spike all samples with the surrogates to monitor recovery. This procedure is described in section 9.5.

9.1.8 The laboratory must spike all extracts with fractionating surrogate compounds prior to the extract being separated into aliphatic and aromatic fractions. The fractionating procedure is described in section 10.3.

9.1.9 The laboratory must spike a minimum of five percent or one per batch, which ever is more frequent of all samples in each matrix, with the MSS (see section 6.8.6) to monitor and evaluate laboratory data quality. This procedure is described in section 9.7.

9.1.10 An auto sampler vial septum should be penetrated and extracted with methylene chloride to evaluate the potential alkane distribution that could occur in re-analyzed extracts. Vial septa should be changed after each analysis.

9.2 To initially establish the ability to generate acceptable precision and accuracy, the laboratory must perform the following operations. Multiple extraction and analysis of the LCSs containing aliphatic and aromatic compounds described in section 6.8.6 is required. The LCS concentrates must be prepared by the laboratory using stock standards prepared from a second source (i.e., other than the source used for calibration). All the LCSs must be prepared, extracted, fractionated and analyzed exactly as a typical environmental sample submitted for analysis.

9.2.1 Aqueous

Prepare seven 1 L aliquots of the well-mixed reagent water spiked with 1.0 mL of MSS from section 6.8.6 and 1.0 mL of the Surrogate Spiking Solution from section 6.8.4. Follow all extraction, fractionation and analytical procedures described in this method.

9.2.2 Soil and Sediment

Prepare seven 10 g aliquots of clean sand (or sodium sulfate) spiked with 1.0 mL of MSS from section 6.8.6 and 1.0 mL of the Surrogate Spiking Solution from section 6.8.4. Follow all extraction, fractionation and analytical procedures described in this method.

9.2.3 For each matrix, calculate the mean recovery (C_{mean}) for each of the aliphatic and aromatic compounds using the seven results. The average percent recovery for each compound must be between ±40% of the true value.

9.2.4 For each matrix calculate the percent relative standard deviation (%RSD) of the seven replicate analyses using the following calculation:

$$\%RSD = \frac{S_{n-1}}{C_{mean}}$$

Where

S_{n-1} = standard deviation (n-1) of the replicates
C_{mean} = mean of the concentration of a compound from the replicates

The %RSD for each compound must be less than or equal to 25%. A higher %RSD is allowed for n-Nonane but the value must be documented.

9.2.5 For each matrix, the FID retention times of the surrogates must match those in the calibration standard as described in section 8.1.1.

9.3 For each analytical batch (up to 20 samples of a similar matrix) the laboratory must analyze a LCS. The LCS shall be prepared by fortifying a reagent water or clean sand (or sodium sulfate) blank with 1.0 mL of the matrix spiking solution. The recoveries of each of the compounds in the LCS must be between 40% - 140%. Lower recoveries are

permissible for n-Nonane but the recoveries must be greater than 25% and must be noted in the case narrative. In addition to the individual recoveries, the recoveries of each of the carbon ranges should be determined and reported. The FID retention times of the surrogates must match the previous calibration as described in section 8.1.1.

9.4 For the same analytical batch described in section 9.3 above, (up to 20 samples of a similar matrix) the laboratory must analyze a LCSD. The LCSD is separately prepared, processed and analyzed in the same manner as the LCS. The recoveries of each of the compounds in the LCSD must be between 40% - 140%. Lower recoveries are permissible for n-Nonane but the recoveries must be greater than 25% and must be noted in the case narrative. In addition to the individual recoveries, the recoveries of each of the carbon ranges should be determined and reported. The Analytical batch precision is determined from the Relative Percent Difference (RPD) of the concentrations (not the recoveries) of the LCS/LCSD pair. The RPDs for the aliphatic and aromatic carbon range concentrations (the sum of the individual compounds' concentrations within a carbon range) must be ≤25%. The FID retention times of the surrogates must match the previous calibration as described in section 8.1.1.

9.5 As a quality control check, the laboratory must spike all samples with the surrogates in section 6.8.3 and calculate the percent recovery (%P) of the Surrogate based on the FID response.

$$\%P = \frac{A_x}{A_s} * 100$$

A_x = Area response of SS in check sample
A_s = Average area response of SS in standard

9.5.1 For the surrogate standards, the laboratory must develop separate accuracy statements of laboratory performance for each matrix. An accuracy statement for the method is defined as Percent Recovery ± Standard Deviation (P ± s). The accuracy statement should be developed by the analysis of four aliquots as described in section 9.2, followed by the calculation of P and s. Alternatively, the analyst may use four data points gathered through the requirement for continuing quality control in section 9.3. The accuracy statements should be updated regularly. The recovery must be within 40% - 140%.

9.5.2 Calculate upper and lower control limits for %R for the surrogate standard in each matrix.

Upper Control Limit (UCL) = P + 3s
Lower Control Limit (LCL) = P - 3s

The UCL and LCL can be used to construct control charts that are useful in observing trends in performance.

9.5.3 The following corrective actions can be taken when the percent recovery of OTP and COD are outside of the recovery range:

9.5.3.1 Check calculations to assure there are no errors.

9.5.3.2 Check instrument performance. Check the sample preparation procedure for loses due to temperature control and surrogate solutions for degradation contamination, etc.

9.5.3.3 Reanalyze the extract if the steps above fail to reveal a problem. If reanalysis yields surrogate recoveries within the stated limits, the reanalysis data should be used.

9.5.3.4 If COD recovery is below the acceptance range and is observed in the aromatic fraction and/or OTP recovery is below the acceptance range and is observed in the aliphatic fraction, then re-fractionate the extract with the remaining 1 mL aliquot of extract and analyze the new extracts.

9.5.3.5 If the surrogate could not be measured because the sample was diluted prior to analysis, then qualify the surrogate recovery. Qualify the out of range surrogate on the data table. No additional corrective action is required.

9.5.3.6 If the steps above fail to reveal a problem, then it may be necessary to re-extract and re-analyze the sample.

9.6 Each field and QC sample must be evaluated for potential breakthrough on a sample-specific basis by evaluating the %recovery of the fractionation surrogates and on a batch-specific basis by quantifying the concentrations of naphthalene and 2-methylnaphthalene in both the aliphatic and aromatic fractions of the LCS and LCSD. (Because naphthalene and substituted naphthalenes are weakly polar, the compounds readily mobilize into the aliphatic extract if excessive amounts of hexane are used to elute the silica gel column. As a result, the aliphatic fraction is monitored for the presence of naphthalene and 2-methylnaphthalene in the LCS and LCSD on a batch basis.) If either the concentration of naphthalene or 2-methylnaphthalene in the aliphatic fraction exceeds 5% of the total concentration for naphthalene or 2-methylnaphthalene in the LCS or LCS duplicate, then fractionation must be repeated on all stored affected sample extracts. (Note the total concentration for naphthalene or 2-methylnaphthalene in the LCS/LCS duplicate pair includes the summation of the concentration detected in the aliphatic and aromatic fractions.)

Example of Naphthalene % Breakthrough Calculation

Naphthalene in aromatic fraction	=	50
Naphthalene in aliphatic fraction	=	1.5
Total Naphthalene concentration	=	51.5
% Naphthalene Breakthrough	=	$1.5 \div 51.5 \times 100$ = 2.9%

(Note: This calculation also may be applied to determine the breakthrough of 2-methylnaphthalene.)

Additionally, if the fractionation surrogate recovery for either compound is outside 40%-140% for any sample extract then fractionation must be repeated on the affected sample.

9.7 Matrix Spike Analysis - The laboratory must, on an ongoing basis, spike and analyze at least 5% of the samples for each matrix being monitored to assess accuracy with the MS. It may be necessary, at the request of the Department, to perform a matrix spike for each matrix from each site even though the frequency may be greater than 5%. The spike is the matrix spiking standard (MSS) defined in section 6.8.6. (If a Matrix Spike Duplicate is requested, then the Relative Percent Difference (RPD) should be $\leq$50.)

9.7.1 Report the recoveries for each of the carbon ranges for each fraction.

9.7.2 The laboratory should establish their own acceptance criteria for % recovery (R) as in section 9.2.3. However, recoveries of 40-140% should be achieved for each compound.

9.8 Sample Duplicate - The laboratory must, on an ongoing basis, analyze 5% of the samples for each matrix in duplicate. Both results are to be reported. (No specific criteria concerning the relative percent difference (RPD) exist at this time. However, results should not differ by more than 50 %.) The laboratory should establish their own acceptance criteria for RPD based on control charts. A matrix spike duplicate may be used if no positive EPH samples are in the batch.

9.9 Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9.10 The laboratory shall determine the method detection limits (MDLs) for the fuels of interest using the methods of 40 CFR 136 Appendix B (13). The MDLs must be confirmed by analyzing a low level standard (2-3 X MDL).

9.11 Vendor-prepared Quality Control Samples may be requested to be both purchased and analyzed by the laboratory. The results are to be within the acceptance limits provided by the vendor for that sample. If acceptable results cannot be obtained then corrective measures should be taken within the laboratory prior to any analysis of environmental samples.

10.0 PROCEDURES

In this method, the extraction procedures for aqueous and soil/sediment samples that have been detailed are manual separatory funnel liquid-liquid extraction (SW-846 Method 3510C) and Soxhlet Extraction (SW-846 Method 3540C), respectively. However, the following alternative extraction procedures listed are acceptable provided the laboratory can demonstrate acceptable performance as described by this method: Aqueous samples may be extracted by Continuous Liquid-Liquid Extraction (SW-846 Method 3520C). Soil/Sediment samples may be extracted by Automated Soxhlet Extraction (SW-846 Method 3541) or Pressurized Fluid Extraction (SW-846 Method 3545A) provided acceptable performance is demonstrated.

10.1 Dissolved Product (Aqueous Samples): Separatory Funnel Extraction

10.1.1 Aqueous samples are extracted using separatory funnel techniques. The separatory funnel extraction scheme described below assumes a sample volume of 1 L. When a sample volume of 2 L is to be extracted, use 250, 100 and 100-mL volumes of methylene chloride for the serial extraction.

10.1.2 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a 2 L separatory funnel. Measure/adjust pH to 2 with 6N HCL. Add 100 ug of surrogates (1 ml of the surrogate spiking solution, section 6.8.3) into the separatory funnel and mix well.

10.1.3 Add 60 mL of methylene chloride to the sample bottle, seal and shake for 30 seconds to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for two minutes with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 5 minutes.

If the analyst must employ mechanical techniques to the complete phase separation, the optimum technique depends upon the sample. The techniques may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Collect the methylene chloride extract in a 250 mL Erlenmeyer flask with a glass stopper.

10.1.4 Add a second 60 mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner. Label the combined extract. Screen the extract (see section 10.4) before concentrating.

10.1.5 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10 mL concentrator tube to a 500 mL evaporative flask.

10.1.6 Pour the combined extract through a solvent rinsed drying column containing about 10 cm of anhydrous sodium sulfate, and collect the extract in the K-D concentrator. Rinse the Erlenmeyer flask and column with 20 to 30 mL of methylene chloride to complete the quantitative transfer.

10.1.7 Add one or two clean boiling chips and attach a three-ball Snyder column to the evaporative flask for each fraction. Prewet each Snyder column by adding about 1 mL of methylene chloride to the top. Position the K-D apparatus in a hot water bath (60^{o}C to 65^{o}C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 minutes. At the proper rate of the distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

10.1.8 Exchange the methylene chloride with hexane by adding 50 ml of hexane to the top of the Snyder column. Concentrate the extract to less than 10 mL as described in 10.1.7, raising the temperature of the water bath, if necessary, to maintain proper distillation.

10.1.9 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with approximately 0.2 mL of hexane. Place the concentrator tube containing the hexane extract onto a nitrogen blowdown apparatus (see section 5.3.9). Adjust the final volume to 1.0 mL with the solvent under a gentle stream of nitrogen. (Note: Caution must be exercised during blowdown to prevent the loss of the lower boiling EPC constituents. The fraction extract volume should never be reduced below 1 mL.)

10.1.10 Add 1 mL of the concentrated fractionation surrogate spiking solution to the 1mL hexane extract. The two mL extract is ready to be cleaned and fractionated using either commercially available or self-packed silica gel SPE cartridges. If cleanup will not be performed immediately, transfer the extract to a Teflon lined screw cap vial and refrigerate.

10.1.11 Determine the original sample volume by refilling the sample bottle to the mark with water and transferring the liquid to a 1000 mL graduated cylinder. Record sample volume to the nearest five mL.

10.2 Sample preparation, soils and sediments: Soxhlet Extraction

10.2.1 Homogenize the soil sample with a solvent-rinsed stainless steel spatula. Weigh about five grams ±.01g of the sample into a tared aluminum pan. Dry at 105 degrees Celsius for 12 hours and calculate the percent solids content (see section 11.4).

10.2.2 The Soxhlet Extraction method USEPA SW-846 Method 3540 is recommended and may be used for all sample types.

10.2.2.1 Blend 10-30g of the solid sample with 10-30g of anhydrous sodium sulfate and place in an extraction thimble. (The sample weight used should be such that, after correction for % moisture, the dry weight of the sample is equivalent to 10 grams. Samples with expected concentrations greater than 2500 mg/Kg may be extracted using a smaller sample size.) The extraction thimble must drain freely for the duration of the extraction period. A glass wool plug above and below the sample in the Soxhlet Extractor is an acceptable alternative for the thimble. Add 100 ug of the surrogate standard spiking solution onto the sample.

10.2.2.2 Place 300 mL of the extraction solvent into a 500-mL round-bottom flask containing one or two clean boiling chips. Attach the flask to the extractor and extract sample for 16-24 hours at 4-6 cycles/hr.

10.2.2.3 Allow the extract to cool after the extraction is complete. Screen the extract before continuing (see section 10.4). Dry and concentrate the extract as in section 10.1.5 through 10.1.9.

10.2.2.4 Add 1 mL of the concentrated fractionation surrogate spiking solution to the 1mL hexane extract. The resultant 2 mL extract is ready to be cleaned and fractionated using either commercially available or self-packed silica gel SPE cartridges. If cleanup will not be performed immediately, transfer the extract to a Teflon lined screw cap vial and refrigerate.

10.3 Extract fractionation

10.3.1 The silica gel cleanup and fractionation step is a critical and sensitive procedure. Small changes in the volumes of eluting solvents, fractionation equipment including the preparation of the silica gel columns and fractionation technique can impact the proportion of the hydrocarbons separated into their respective aliphatic and aromatic fractions. Care and attention is required to ensure acceptable results.

Each sample fractionation requires 1 mL of sample extract. As the final volume of the extract prior to fractionation is 2 mL, an additional fractionation is available should it be required. For example, if the original fractionation yields unacceptable breakthrough of naphthalene and/or unacceptable recoveries for the fractionation surrogate standards, the remaining 1 mL extract may have to undergo fractionation.

A commercially available 5g/20mL SPE cartridge may be used. Alternatively, columns packed with activated silica gel by the laboratory may be used. The use of activated silica gel is described in USEPA SW-846 Method 3630C.

Silica gel columns/cartridges must never be overloaded. Overloading may result in the premature breakthrough of the aromatic fraction. It is recommended that for a 1mL extract fractionated on a 5g cartridge, the extract should contain no more than 5 mg total EPH. (This equates to 25000 ug/mL in the extract or 2500 mg/Kg in the sample.)

10.3.2 Demonstrate Fractionation Capability

Every new lot of silica gel/SPE cartridges must be evaluated with the Fractionating Check Solution to establish the optimum volume of hexane to efficiently elute aliphatic hydrocarbons while not allowing significant aromatic hydrocarbon breakthrough. The amount of hexane used is critical and is to be optimized prior to the analysis of any samples. Excessive hexane can cause the elution of lighter aromatics into the aliphatic fraction. Insufficient hexane could result in low recoveries of the aliphatics. The volume of hexane used should not exceed 20 mL. A fractionation check solution (FCS) is prepared in hexane containing all the compounds listed in section 6.8.9 at a nominal concentration of 200 ng/uL each component. To demonstrate proper fractionating capability, at least four 1mL replicates of the FCSs must be fractionated using the procedures detailed in 10.3.3 below and analyzed. The mean measured concentration (C_{xmean}) of the individual fractionation compounds is determined using the following equation:

$$\%\,Mean\ Recovery = \frac{C_{x\,mean} - True\,Concentration}{True\,Concentration} * 100$$

Where $C_{x\,mean} = \frac{C_1 + C_2 + C_3 + ... + C_n}{n}$

For each analyte included in the FCS, the % mean recovery must be between 40% and 140%. Lower recoveries are permissible for n-Nonane. However, if recovery is <25% then the problem must be found and the fractionation check repeated.

10.3.3 Fractionate the extract into separate aromatic and aliphatic components.

10.3.3.1 Prepare the column by placing about 1 cm of glass wool (moderately packed) at the bottom of the column. Make sure the stopcock turns smoothly.

10.3.3.2 Fill the column with a slurry of 5 g activated silica gel in about 10 ml methylene chloride. Tap the side of the column to assure uniform packing. Top the column with approximately 1 to 2 cm sodium sulfate.

10.3.3.3 Rinse the column/SPE cartridge with 30 ml methylene chloride if there are concerns of contaminants in the silica gel. Let the solvent flow through the column until the head of the solvent is just above the top of the column packing. Discard the eluted methylene chloride.

10.3.3.4 Rinse the column with 30 mL of hexane (60 mL if pre-rinsed with methylene chloride). Let the hexane flow through the column until

the head of the column is just above the frit. Close the stopcock to stop flow. Discard the hexane.

10.3.3.5 Load 1 mL of the combined sample extract/fractionation surrogate solution (from section 10.1.10 or section 10.2.2.4) onto the column. Open the stopcock and start collecting the elutant immediately in a 25 mL flask labeled "aliphatics."

10.3.3.6 Just prior to the exposure of the column frit to air, elute the column with an additional 19 mL of hexane so a total of 20 mL of hexane has passed through the column. (It is essential that "plug flow" of the extract be achieved through the silica gel column/cartridge.) Hexane should be added in 1 to 2 mL increments with additions occurring when the level of solvent drops to a point just prior to exposing the column frit to air. The use of a stopcock is required. Ensure that the silica gel is uniformly packed in the column. The technician must be aware of any channeling, streaking or changes in the silica gel matrix during fractionation. If any occurs, it is probable that procedure shall have to be repeated with another 1 mL aliquot.

10.3.3.7 Following the recovery of the aliphatic fraction, elute the column with 20 mL methylene chloride. Collect the elutant in a 25 mL volumetric flask. Label this fraction aromatics.

10.3.3.8 Transfer the contents of the aliphatic and aromatic volumetric flasks into separate, labeled graduated concentrator tubes. Concentrate each of the extracts to a final volume of 1 mL under a gentle stream of nitrogen. Analyze each of the extracts separately.

10.3.3.9 Analyze the extracts separately.

10.3.3.10 The recoveries of the fractionation surrogates must be within 40% - 140%. If the fractionation surrogate recovery is outside 40% - 140% then fractionation must be repeated on the affected sample.

10.4 Preliminary Analysis of Extracts (Screening)

To minimize the frequency of sample reanalysis because the extract concentrations exceed the quantitation limits, screening of the extract prior to fractionation is recommended.

10.4.1 Adjust the chromatograph for maximum sensitivity.

10.4.2 Inject 1 uL of the sample extract using an auto sampler.

10.4.3 A complete profile of the extract should be obtained without saturating the detectors. The largest peak should be within the linearity of the instrument for that compound. If the response is too high, the extract should be diluted accordingly.

10.5 Chromatographic Analysis

10.5.1 One milliliter of extract ready for analysis should be transferred to a one mL GC auto sampler vial.

10.5.2 Inject 1 to 4 uL of extract using an autosampler device or the solvent plug method.

10.5.3 Instrument Performance

10.5.3.1 All of the peaks contained in the standard chromatograms must be sharp and symmetrical. Peak tailing must be corrected.

10.5.3.2 Check the precision between consecutive QC check samples. A properly operating system should perform with an average relative standard deviation of less than 10%. Poor precision is generally traceable to pneumatic leaks.

10.5.3.3 Monitor the retention time for each analyte using data generated from calibration standards. If individual retention times vary by more than ±3 standard deviations (see section 7.1.1) over a twelve hour period, then the source of retention data variance must be corrected before acceptable data can be generated.

10.5.3.4 The instrument sensitivity must be maximized. Injection of 2ul of a 1ng/ul hydrocarbon standard should yield a detector signal-to-noise ratio of at least 5:1 for the individual alkanes.

10.6 Analysis Sequence

10.6.1 This method uses a 24 hour clock or a 20 sample analytical batch, whichever time is shorter. The time sequence begins with the analysis of the first initial calibration standard or continuing calibration standard and ends with a closing calibration standard. The calibration curve must be verified every 24 hours or 20 samples, whichever is more frequent.

10.6.2 Sequence (for each fraction)

1. Instrument Blank.
2. Analytical Batch Opening Initial Calibration or mid range Continuing Calibration (required).
3. Method Blanks (required).
4. Extraction Batch LCS (required).
5. Extraction Batch LCS Duplicate (required).
6. Samples (up to 20).
7. Matrix Spike (required).
8. Matrix Spike Duplicate (if requested).
9. Closing mid-range Continuing Calibration Standard after 20 samples (at a minimum of once every 24 hours) and at the end of an analytical batch (required). This standard may be used as the Analytical Batch Opening Continuing Calibration for the next analytical batch if batches are processed continuously.

11.0 CALCULATIONS

11.1 Concentration of Petroleum Hydrocarbons

11.1.1 To calculate the concentration of carbon ranges in the sample, the area response attributed to the petroleum must first be determined. This area includes all of the resolved peaks and the unresolved "envelope." This total

area must be adjusted to remove area response of the solvent, surrogates and the GC column bleed.

11.1.2 Establishing the baseline

11.1.2.1 Column bleed is defined as the reproducible baseline shift that occurs during temperature programming of the GC column oven. The instrument baseline must be established by the direct injection of a system solvent blank. The injection of an air blank or activation of a temperature programmed chromatographic run without the injection of any material would be used to verify that the system noise is not attributable to solvent contamination. The instrument must be run at the actual operating conditions used to analyze all standards and samples. A system solvent blank injection should be analyzed at the beginning of the day and at a minimum after every 24 hours to determine the baseline response. The baseline is then set at a stable reproducible point just before the solvent peak. This baseline should be extended horizontally to the end of the run. When quantifying on peak areas, collective peak area integration for the fractional ranges must be from baseline (i.e., must include the unresolved complex mixture "hump" areas). However, the unresolved "hump" areas are not to be included in the integration of individual compounds such as surrogates.

11.1.2.2 The baseline for the sample should be set in the same manner. The area in the sample will contain the area attributed to petroleum and that attributable to the baseline. Aliphatic and aromatic hydrocarbon carbon range data for the area between C9 and C40 may be corrected by the automatic or manual subtraction of the baseline area from the system solvent blank. Correction in this manner is not recommended or preferred but permissible in cases where reasonable steps have been taken to minimize or eliminate excessive baseline bias associated with analytical system noise.

11.1.2.3 If baseline correction is used, then the baseline must be re-established for every analytical batch by the analysis of a system solvent blank.

11.1.2.4 As the concentration of any carbon range in the sample approaches the quantitation limit, the baseline correction becomes more critical.

11.2 External standard calibration - The concentration of each carbon range for each fraction in the sample is to be determined by calculating the amount of analyte injected, from the peak response, using the calibration factor. The area of the surrogates must be subtracted from their corresponding carbon range summed area. Additionally, any areas associated with naphthalene and/or 2-methylnaphthalene in an aliphatic carbon range are to be subtracted from the appropriate aliphatic carbon range summed area prior to calculating the calibration factors. The concentration of a specific carbon range is calculated as follows:

11.2.1 Aqueous samples

$$C(ug/L) = \frac{(A)(D)(V_e)}{CF(V_s)}$$

Where:

C = Concentration of each compound or hydrocarbon carbon range, ug/L

A = Area response of each compound or carbon range to be measured.

D = Dilution Factor

V_s = Volume of sample extracted, mL

V_e = Final volume of the extract, uL

CF = Calibration Factor of each compound or carbon range for each fraction (see section 8.1.2)

Where:

$$CF = \frac{Peak\ Area\ or\ Summed\ area\ of\ peaks\ in\ carbon\ range}{Total\ concentration\ injected\ (ng/uL)}$$

11.2.2 Nonaqueous - Soils/Sediments/Sludge

$$C(ug/g) = \frac{(A)(D)(V_e)}{CF(S)}$$

Where:

C = Concentration of each compound or hydrocarbon carbon range, ug/g (dry weight basis)

A = Area response of each compound or carbon range to be measured.

D = Dilution Factor

Ve = Final volume of the extract, uL

CF = Calibration Factor of each compound or carbon range for each fraction (see section 8.1.2).

Where:

$$CF = \frac{Summed\ area\ or\ peaks\ or\ Summed\ area\ of\ peaks\ in\ carbon\ range}{Total\ concentration\ injected\ (ng/uL)}$$

S = Dry sample weight, mg

11.2.3 Total EPH Concentration = Total of the 4 Aromatic carbon ranges and 4 Aliphatic carbon ranges.

11.3 Percent Recovery of Surrogate Standard(s)

Percent recovery based on External Calibration

$$\%\,SS\,Recovery = \frac{C_{of}}{C_{ot}} * 100$$

Where:

C_{of} = Concentration of surrogate found
C_{ot} = Concentration of surrogate added

11.4 Percent Solids (P)

$$P = \frac{D_s}{T_s} * 100$$

Where:

D_s = Weight dry Sample, g
T_s = Weight wet Sample, g

11.5 Dry Weight (S)

$$S = \frac{Wet\ Weight\ x\ P}{100}$$

Where:

P = Percent solids

12.0 REPORTING REQUIREMENTS AND DELIVERABLES

The following information must be provided to the Department upon request. The Laboratory must keep this information on file and available for inspection by the Department as per N.J.A.C. 7:18 (12).

12.1 Chain of Custody Documents.

For every sample submitted to the laboratory, both field (external) and laboratory (internal) chain of custody documents MUST be provided at the end of the final data report. The chain of custody must show the signatures of the sample custodian, extraction supervisors and any other personnel who handled the sample. It must clearly track the movement of the sample through the laboratory by showing the relinquishing and acceptance of the sample by each person. Tracking may be accomplished electronically if laboratory personnel have user specific password-protected access to their respective LIM systems that track sample movement through the laboratory.

12.2 Methodology Review

The laboratory shall provide a brief narrative outlining the essential points of each method actually employed in the analysis of the samples submitted to the laboratory.

12.3 Non-Conformance Summary Report

The laboratory shall describe in narrative and/or tabular form any item which does not conform to the requirements of this method. This shall include but is not limited to a discussion of missed holding times, failed Quality Assurance/Quality Control criteria, sample matrix effects on the analysis, sample dilutions, re-analyses, corrective actions taken and deviations from the analytical method specified on the analytical request form or the preparative methods permitted.

12.4 Sample Data Package - must contain the following information. The information should be provided in the following sequence.

12.4.1 Quantitative Sample Results Summary (uncorrected for blank), Blank Results and Method Detection Limits. Results for each of the concentrations calculated for the 8 carbon ranges plus a total EPH concentration must be provided.

12.4.2 Quantitation Reports. All field samples, QC samples, standards and blanks must have the following information provided:

12.4.2.1 date collected.
12.4.2.2 date received.
12.4.2.3 date extracted.
12.4.2.4 date analyzed.
12.4.2.5 time analyzed.
12.4.2.6 dilution factor.
12.4.2.7 % Moisture (or % solids).
12.4.2.8 Concentrations of individual peaks and/or carbon ranges.

12.4.3 Sample Chromatograms

The chromatograms must be clearly labeled with the following information:

12.4.3.1 Sample identification number.
12.4.3.2 Volume injected.
12.4.3.3 Date and time of injection.
12.4.3.4 GC Column identification.
12.4.3.5 GC instrument identification - exact instrument employed.
12.4.3.6 Carbon ranges identified, either directly above the peak or on a printout of retention times, if the retention times are printed on chromatograms.
12.4.3.7 Surrogates labeled.
12.4.3.8 Fractionation Surrogates labeled.
12.4.3.9 Analyst signature.

12.5 Quality Control Summary - must contain the following items:

12.5.1 Surrogate Recoveries (for all field samples and QC samples) including fractionation and extraction surrogates.
12.5.2 QC Check Sample Results (if analyzed).
12.5.3 LCS Results.
12.5.4 LCSD Results.
12.5.5 Method Blank Summary.
12.5.6 Matrix Spike Summary.
12.5.7 Matrix Spike Duplicate Summary (if requested).
12.5.8 Duplicate Sample Results Summary.

12.5.9 Percentage of total naphthalene and 2-methylnaphthalene concentrations detected in the aliphatic fractions of the LCS/LCSD.
12.5.10 Fractionation Check Solution results.

12.6 Standard Data Packages - must contain the following items:

12.6.1 Initial Calibration Data Summary.
12.6.2 Continuing Calibration Data Summary.
12.6.3 Chromatograms of Standards.
12.6.4 Quantitation Reports.
12.6.5 Summary of retention times of each identified marker compound used to define the beginning and end of each carbon range for each fraction.

12.7 Raw QC Data Package - additionally must contain the following items:

12.7.1 Blank Chromatograms.
12.7.2 QC Check Sample Chromatograms (if analyzed).
12.7.3 LCS/LCSD Chromatograms.
12.7.4 Quantitation Reports.

12.8 Raw Sample Data package - must contain the following items:

12.8.1 Sample chromatograms.
12.8.2 Quantitation reports containing at a minimum the retention times and associated areas of all individual chromatographic peaks from the analysis.

REFERENCES

1. Method for the Determination of Extractable Petroleum Hydrocarbons (EPH), Massachusetts Department of Environmental Protection; Division of Environmental Analysis, Office of Research and Standards, Bureau of Waste Cleanup, May 2004, Revision 1.1.

2. Method for the Determination of Extractable Petroleum Hydrocarbons (EPH) Fractions, Washington State Department of Ecology, June 1997.

3. Leaking Underground Fuel Tank, Task Force "Leaking Underground Fuel Tanks Field Manual," Appendix C, State Water Resources Control Board, Sacramento, CA 1988.

4. U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste -- Physical Chemical Methods, Office of Solid Waste, Washington, DC, Publication SW846, 3rd ed. update III 1996.

5. Florida Department of Environmental Protection, "Method for Determination of Petroleum Range Organics," Method #FL-PRO, rev.1a, March 14, 1997.

6. Miller, M., "Quantitation of Semi-Volatile Petroleum Products in Water, Soil, Sediment, and Sludge," NJDEP OQA-QAM-025-02/08.

7. ASTM, "Comparison of Waterborne Petroleum Oils by Gas Chromatography," Method D3328-90, Annual Book of ASTM Standards, Volume 11.01, Philadelphia, PA, 1990.

8. Staff, Oil Spill Identification System, Report No. GCD-52-77, U.S. Coast Guard R & D Center, page D1, National Technical Information Center, Springfield, VA 1977.

9. "OSHA Safety and Health Standards, General Industry," (29CFR1910), Occupational Safety and Health Administration, OSHA 2206 (Revised, January 1976).

10. "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.

11. "Chromatography Products," RESTEK; Bellefonte, PA, 2006.

12. New Jersey Department of Environmental Protection, "Regulations Governing Laboratory Certification and Standards of Performance," N.J.A.C. 7:18.

13. U.S. Environmental Protection Agency, Federal Register, 40CFR136, Appendix B, Volume 49, No. 209, July 1, 1990.

LIST OF MAJOR METHOD CHANGES IN THIS REVISION

The compounds n-octane and toluene and the surrogate chlorobenzene have been removed from the method.

Carbon ranges have been reduced from 5 ranges per fraction to 4 ranges per fraction. As such the ranges are: The four EC number ranges for the aliphatic fractions are: EC9 to EC12, EC12 to EC16, EC16 to EC21 and EC21 to EC40 and the four carbon number ranges for the aromatic fractions are: EC10 to EC12, EC12 to EC16, EC16 to EC21 and EC21 to EC36.

The dynamic range was redefined in section 2.3.

A listing of the target aliphatic and aromatic compounds was moved from section 6.8 to section 2.4.

Clean sand was added as a matrix that may be used for the fortification QC samples in section 6.6.

The standards and solutions (and concentrations thereof) used throughout the method were more clearly defined in section 6.8.

All issues addressing sample collection, preservation and storage were moved from the end of section 9 and were combined in section 7.0.

The calibration procedures in section 8.0 were modified such that calibration factors, percent difference calculations and percent relative standard deviation calculations must be performed for the individual compounds in the standards in addition to the same information required for the carbon ranges. Acceptance criteria for the individual compounds were included.

Procedures for handling contamination from carryover were embellished in section 9.1.5.

The procedures detailing the initial demonstration of precision and accuracy in section 9.2 require the analysis of seven replicates, up from four. Additionally, the procedures have been more clearly defined.

The evaluation of potential breakthrough during the fractionation step was added in section 9.6.

The use of methods other than separatory funnel extraction and Soxhlet Extraction were added in section 10.0. These methods are Continuous Liquid-Liquid Extraction (SW-846 Method 3520C) for water and Automated Soxhlet Extraction (SW-846 Method 3541) or Pressurized Fluid Extraction (SW-846 Method 3545A) for soil (provided acceptable performance is demonstrated).

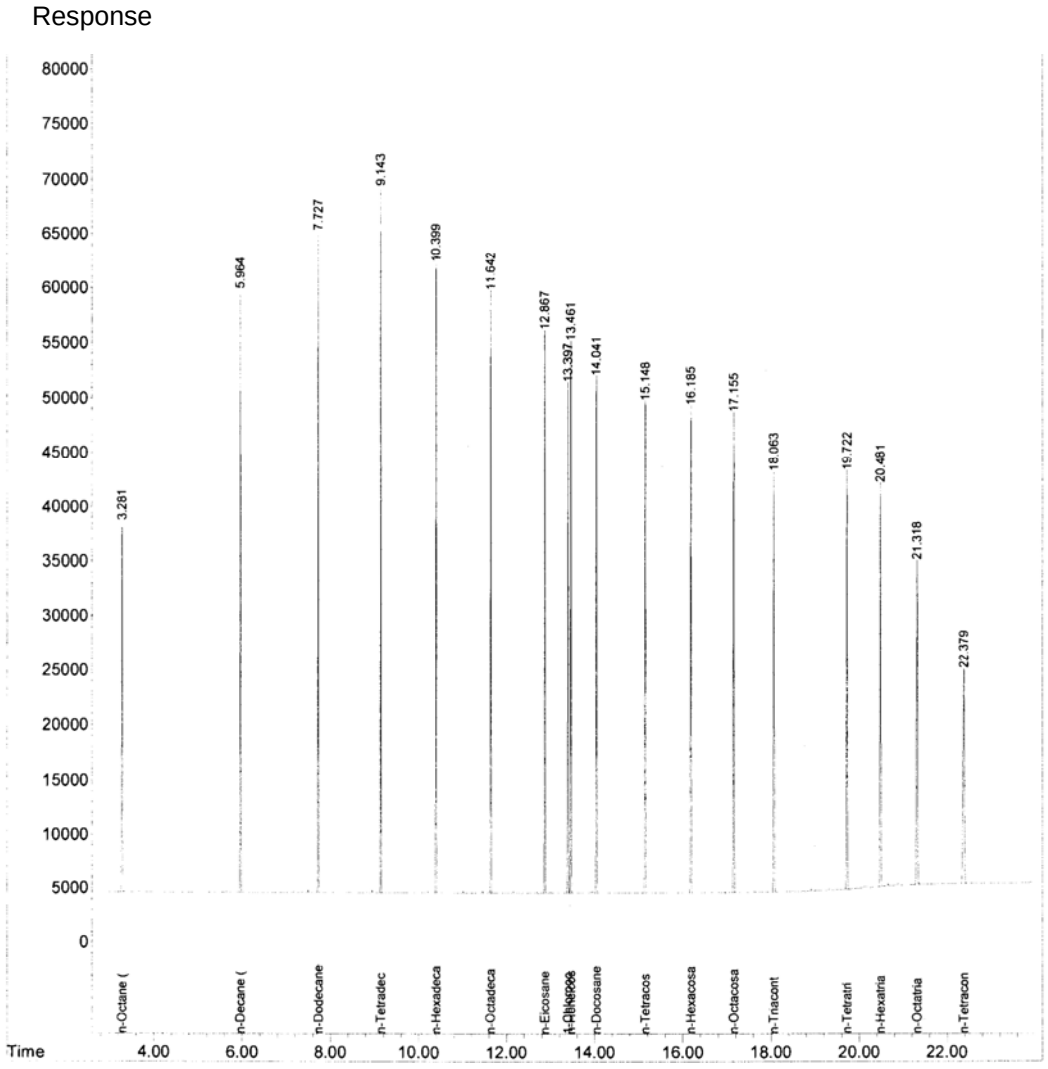
The demonstration of fractionation capability listed in section 10.3.2 was more clearly defined.

The equations used to determine concentrations were revised to include the concentration calculations of individual compounds.

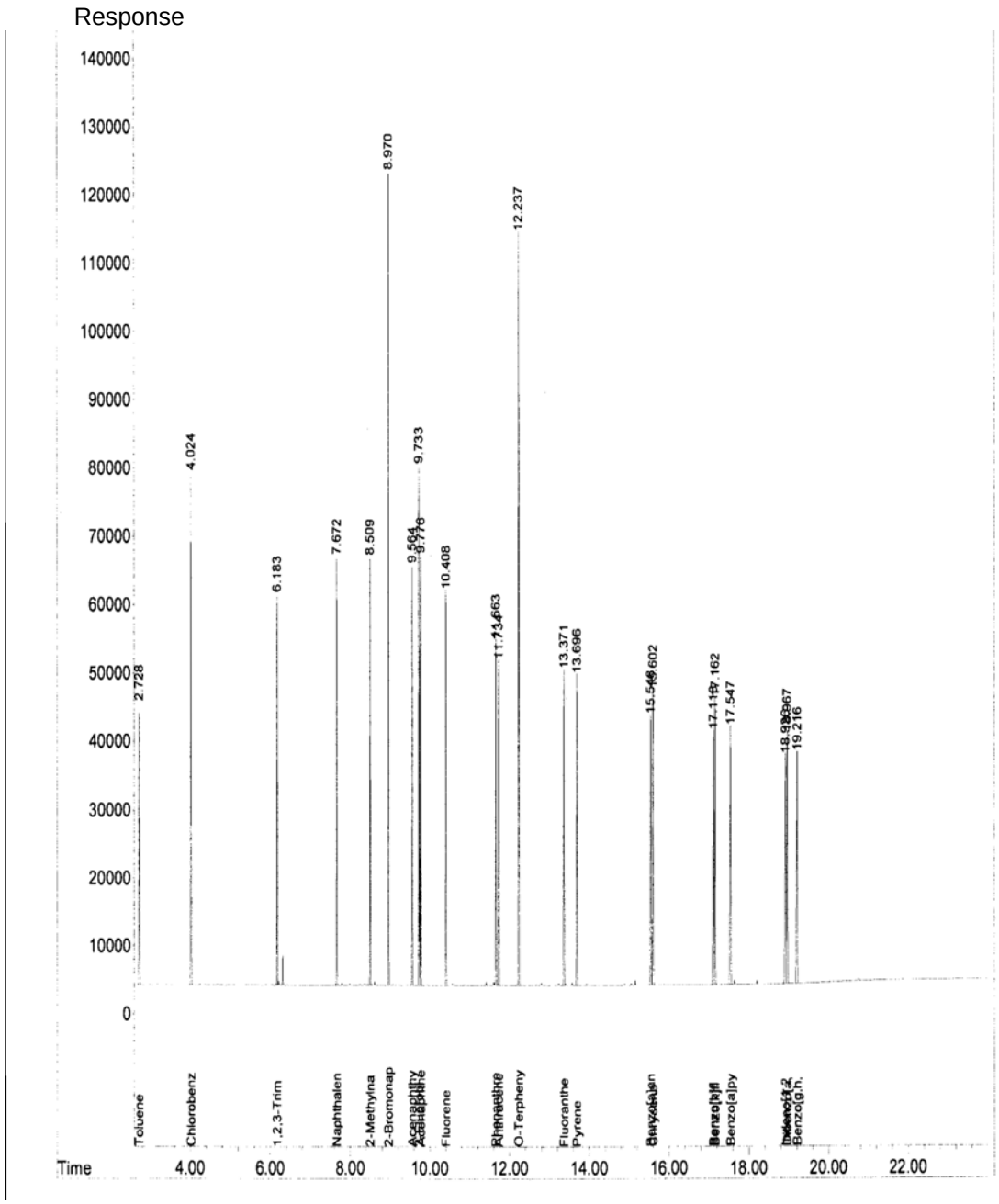
The terminology used to describe the types of chain of custody documents was clarified.

EXAMPLE CHROMATOGRAMS

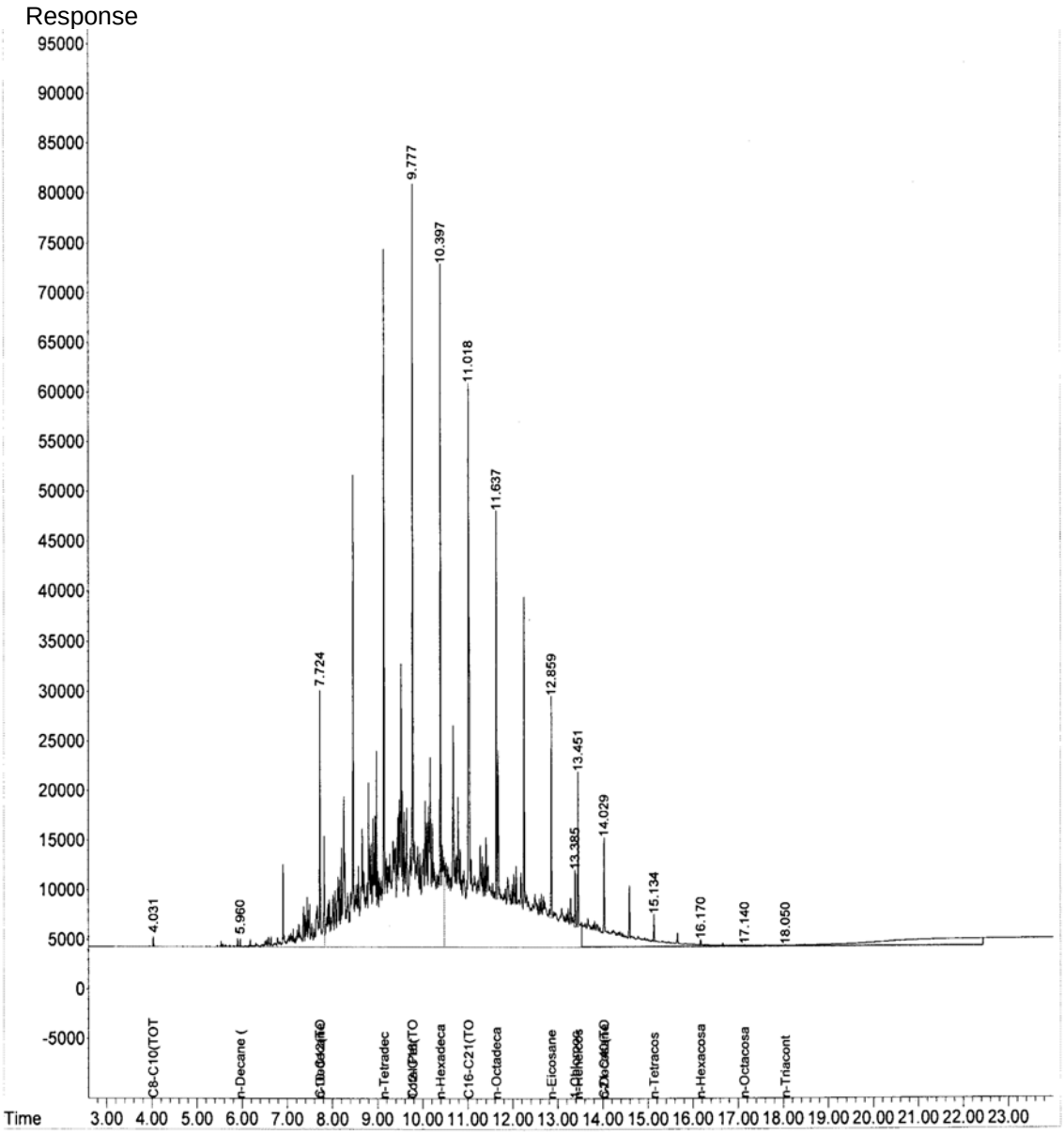
Aliphatic Standard (Each component at 100 mg/Kg)



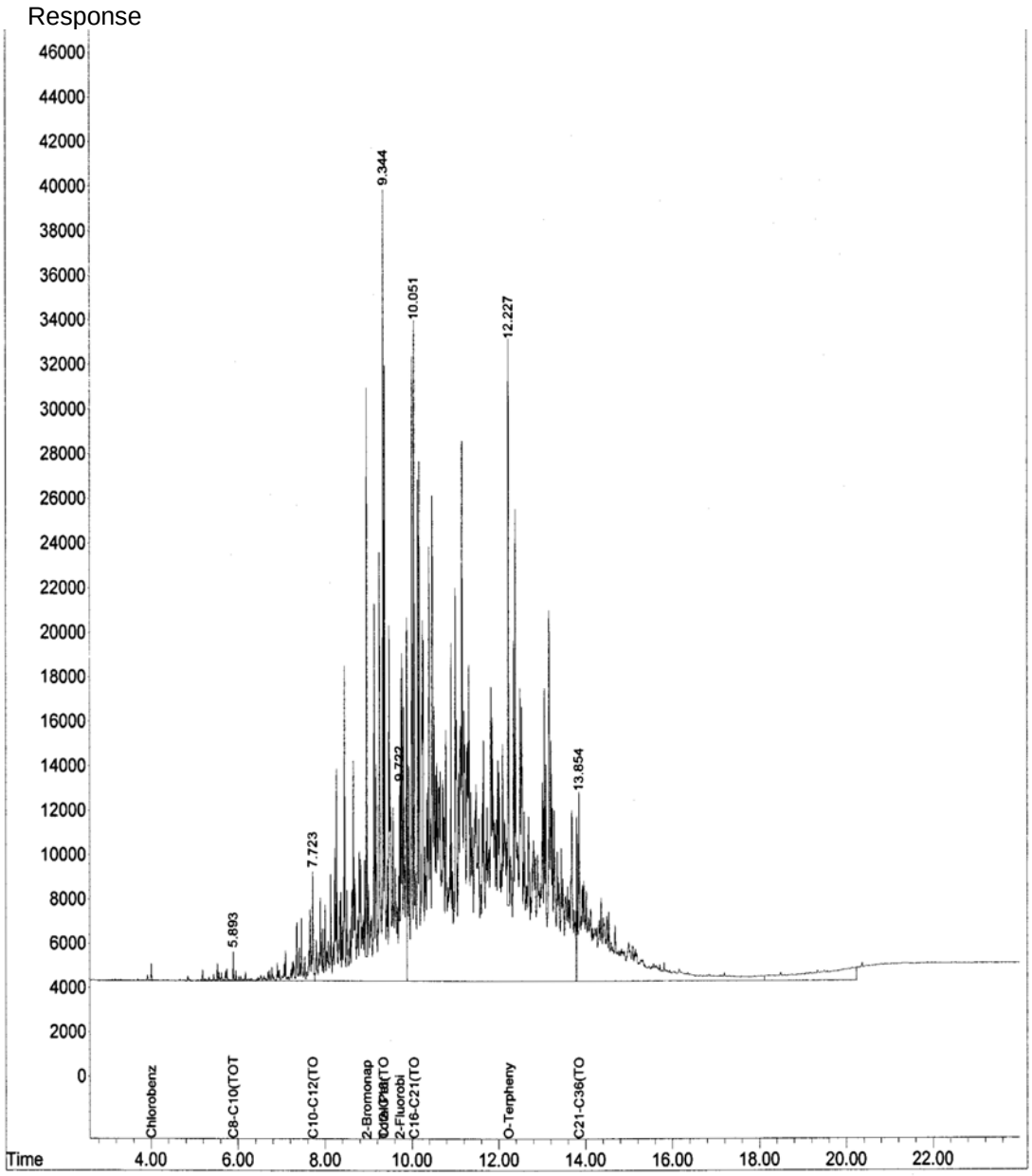
Aromatic Standard (Each component @ 100 mg/Kg)



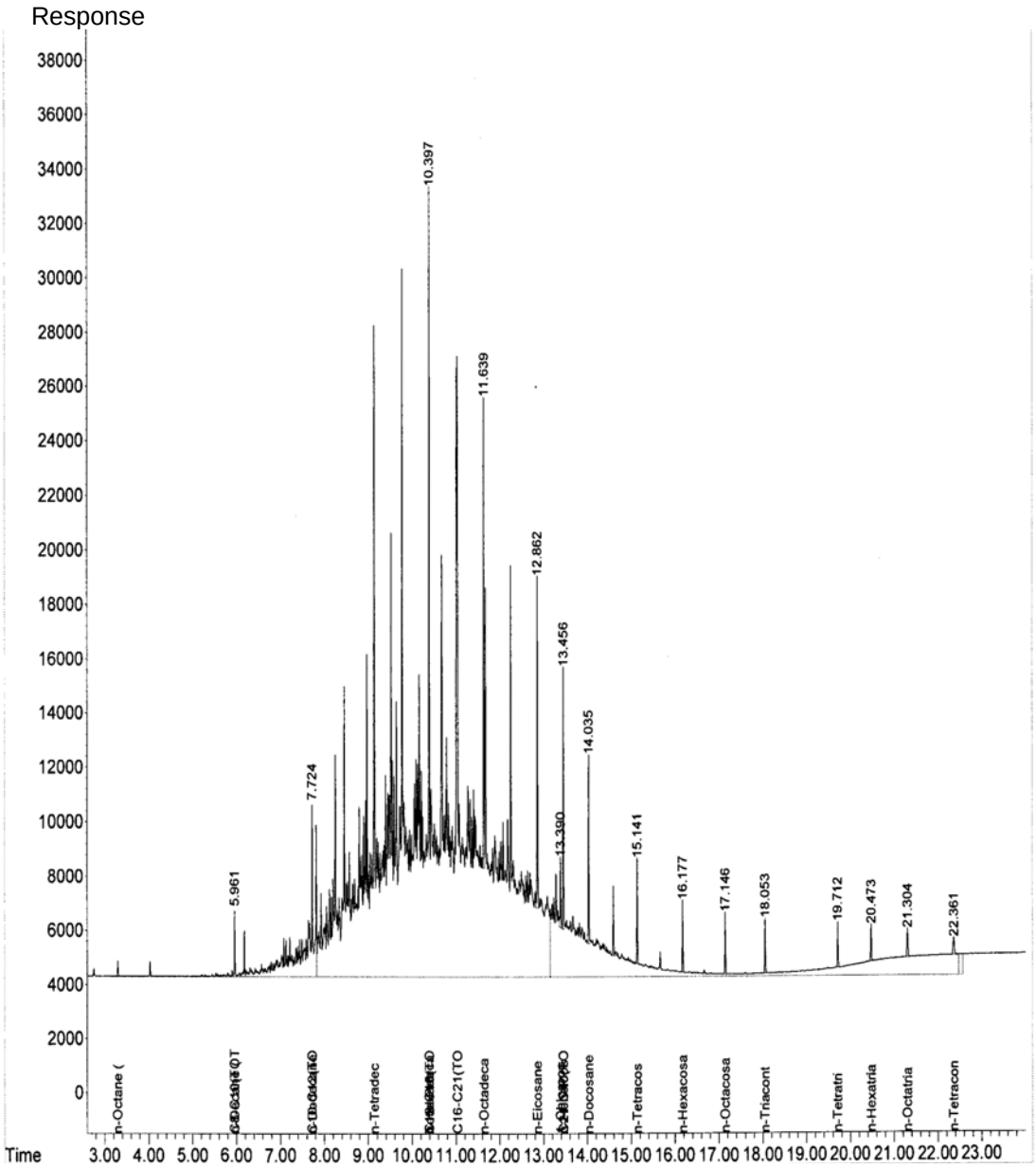
Soil Sample
Aliphatic Fraction
Total EPH Concentration @ 5800 mg/Kg



Soil Sample
Aromatic Fraction
Total EPH Concentration @ 5800 mg/Kg



Matrix Spike
Soil Sample
Aliphatic Fraction



Matrix Spike
Soil Sample
Aromatic Fraction