# New Jersey Extractable Petroleum Hydrocarbons (NJ EPH)

Reference Method No.: Analysis of Extractable Petroleum Hydrocarbons (EPH) in Aqueous and Soil/Sediment/Sludge Matrices, New Jersey Department of Environmental Protection Site Remediation Program, Extractable Petroleum Hydrocarbons Methodology Version 3.0, August 2010 Revision 3.

## 1. Scope and Application

**Matrices:** Water, Soil, Sediment, and Sludge

**Definitions:** Refer to Alpha Analytical Quality Manual.

This method utilizes a gas chromatograph 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.

Quantitative analysis of environmental samples for residues from commercial petroleum products such as crude oil, diesel fuel, waste oil, fuels oils Nos. 2-6, lubricating oil, processed oils and bunker fuel.

*The method is not to 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.*

The FID response produces extractable petroleum hydrocarbon chromatograms that can be used to calculate concentrations of specified carbon ranges for both aliphatic and aromatic fractions. This method provides results for specific carbon number ranges in both aliphatic and aromatic fractions of TPH thereby providing a more accurate assessment of potential health risk at environmental sites.

This method also provides an option where extracts from samples may be analyzed without having to be fractionated.

The data report packages present the documentation of any method modification related to the samples tested. Depending upon the nature of the modification and the extent of intended use, the laboratory may be required to demonstrate that the modifications will produce equivalent results for the matrix. Approval of all method modifications is by one or more of the following laboratory personnel before performing the modification: Area Supervisor, Department Supervisor, Laboratory Director, or Quality Assurance Officer.

This method is restricted to use by or under the supervision of analysts experienced in the operation of the GC and in the interpretation of GC data. Each analyst must demonstrate the ability to generate acceptable results with this method by performing an initial demonstration of capability, analyzing a proficiency test sample and completing the record of training.

After initial demonstration, ongoing demonstration is based on acceptable laboratory performance of an annual proficiency test sample. A major modification to this procedure requires demonstration of performance. The identification of major method modification requiring performance demonstration is directed by the Quality Assurance Officer and/or Laboratory Director on a case-by-case basis.

Parameter List:

| Parameter | CAS |
|---|---|
| C9-C12 Aliphatic Hydrocarbons | - |
| C12-C16 Aliphatic Hydrocarbons | - |
| C16-C21 Aliphatic Hydrocarbons | - |
| C21-C40 Aliphatic Hydrocarbons | - |
| C10-C12 Aromatic Hydrocarbons | - |
| C12-C16 Aromatic Hydrocarbons | - |
| C16-C21 Aromatic Hydrocarbons | - |
| C21-C36 Aromatic Hydrocarbons | - |
| Total EPH | - |
| Total EPH (unfractionated) | - |

# 2. Summary of Method

Petroleum residues are extracted with methylene chloride, dried over sodium sulfate, solvent exchanged into hexane, and concentrated in a Kuderna-Danish apparatus. However, if a non-aqueous sample is known to be contaminated with #2 fuel/diesel or the concentration of a non-#2 fuel/diesel petroleum product in a nonaqueous sample has been determined by this method to be below the number generated by the EPH calculator when it is assumed that 100% of the contamination is in the carbon range with the most conservative toxicity factor (as of June 1, 2010, the number is 1700mg/Kg, subject to change), then solvent exchange and fractionation are not required. Additionally, aqueous samples are not required to undergo solvent exchange and fractionation. Quantitation for non-fractionated samples is performed using the total area of all peaks present and dividing the chromatography into the eight carbon ranges is not required. For all other instances, 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.

## 2.1 Method Modifications from Reference

None.

# 3. Reporting Limits

Reporting Limits are listed in Table 1.

# 4. Interferences

**4.1** 4.1 High purity reagents are used to minimize interference problems.

**4.2** Only high purity gases are used in the GC system to eliminate this source of possible contamination. The air and hydrogen (carrier gas – 99.999%, and detector make-up gas) are certified by the gas supplier.

**4.3** Preventive instrument maintenance is performed routinely, and whenever highly contaminated extracts are analyzed that could result in chromatographic interferences or result in degradation of system performance. Section 9.7 details the maintenance steps.

**4.4** Glassware must be scrupulously cleaned. This procedure is detailed in the extraction SOPs. Store dry glassware in a clean environment.

**4.5** The leaching of plasticizers and other compounds have been observed from commercially available silica gel cartridges used to fractionate EPH sample extracts. This possible source of contamination is continuously monitored and documented by analysis of Laboratory Method Blanks.

**4.6** Contamination by carry-over can occur whenever high-concentration and low-concentration samples are sequentially analyzed. Whenever an unusually concentrated sample is encountered, it must be followed by the analysis of a solvent blank to check for possible carry-over. If this is not done and the sample analyzed immediately following the high-concentration sample is free from contamination, then it may be assumed that carry-over is not an issue. However, if this sample did detect analytes which were present in the unusually concentrated sample, reanalysis is required for all samples analyzed after this highly concentrated sample which detected similar analytes.

**4.7** Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interference will vary considerably from one source to another depending upon the nature and diversity of the site being sampled. The silica gel SPE cleanup procedure is used to overcome many of these interferences, but some samples may require additional cleanup approaches that are beyond the scope of this method.

**4.8** Certain organic contaminants mixed with petroleum product releases, including chlorinated hydrocarbons, phenols, and phthalate esters, will be quantitated as Extractable and Total Petroleum Hydrocarbons. If necessary and/or desirable, additional sample cleanup and/or analytical procedures may be employed to minimize or document the presence of such compounds.

**4.9** Because of their weakly polar nature, naphthalene and substituted naphthalenes are readily fractionated into the aliphatic extract if excessive amounts of hexane are used to elute the silica gel cartridge/column. Because these compounds constitute a significant percentage of the water-soluble fraction of fuel oils, this occurrence is especially problematic in the analysis of water samples. For this reason, the method requires the evaluation of the aliphatic fraction for the presence of naphthalene and 2-methyl-naphthalene in the LCS/LCSD pair on a per batch basis. The fractionation surrogate, 2-Bromonaphthalene, is used to monitor sample-specific fractionation efficiency.

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

**4.11** Before processing samples an instrument blank is analyzed to show the system is interference free.

# 5. Health and Safety

The toxicity or carcinogenicity of each reagent and standard used in this method is not fully established; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. A reference file of material safety data sheets is available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available in the Chemical Hygiene Plan.

All personnel handling environmental samples known to contain or to have been in contact with municipal waste must follow safety practices for handling known disease causative agents.

**5.1** Lab coats, safety glasses, and gloves must be worn when handling samples, extracts, standards or solvents.

**5.2** All solvent and extract transfers must be handled in the vented bench area in the GC laboratory.

**5.3** All stock standards, working standards, and vialed sample extracts must be placed into the waste bucket in the lab, for future disposal by the Hazardous Waste Manager. The container must be labeled properly with hazard warning labels indicating the container contents.

**5.4** Bottles containing flammable solvents must be stored in the flammables cabinet.

# 6. Sample Collection, Preservation, Shipping and Handling

## 6.1 Sample Collection

Aqueous samples are collected in two 1L amber glass jars with teflon-lined lids. Solid samples are collected in 250mL wide-mouth amber glass jars with teflon-lined lids. All containers are purchased pre-cleaned and certified from commercial vendors.

## 6.2 Sample Preservation

Both aqueous and solid samples are then preserved by packing in coolers with ice or ice packs, to maintain a temperature of 4 ±2 $^{o}$C. Additionally, aqueous samples are preserved at the time of sampling by the addition of approximately 5mLs of 1:1 HCl. The sample pH must be less than 2.0 after addition of the acid. Upon receipt at the laboratory, the samples are transferred into sample storage refrigerators to maintain at a temperature of 4 ±2 $^{o}$C.

## 6.3 Sample Shipping

No specific shipping requirements.

### 6.4 Sample Handling

Aqueous and soil/sediment samples must be extracted within 14 days of sample collection, and be analyzed within 40 days of the extraction date.

## 7. Equipment and Supplies

**7.1 Gas Chromatograph, Hewlett Packard 6890:** An analytical system complete with gas chromatograph configured for split-splitless injection and all required accessories including autosampler syringes, analytical columns, gases, and flame ionization detectors (FID). The systems used for this analysis are configured with dual injectors/dual columns for simultaneous injection and analysis of both the aliphatic and aromatic extracts.

**7.2 Data System:** A computer system is interfaced to the GC for collection of data. Chemstation software is used for data acquisition and data reduction and processing.

**7.3 GC Columns:** RTx-5MS, 30 m x 0.32 mm ID fused silica capillary column, 0.25 µm film thickness. Alternative columns may be used as long as the method performance criteria can be met.

**7.4 Microsyringes:** 10µL, 100µL, 250µL, 500µL and 1000µL

**7.5 Volumetric Flasks:** 10mL and 25mL, used for standard preparation.

**7.6 Disposable Borosilicate Pipets**

**7.7 Vials:** 2 mL clear glass, crimp-top and screw-cap.

**7.8 Silica Gel Fractionation Tubes:** Typical vendor and catalog number: Phenomenex, Catalog Number AHO-8226

**7.9 Silica Gel:** Typical vendor and catalog number: VWR, Catalog Number TX4694MAAA

## 8. Reagents and Standards

Reagent grade or pesticide grade chemicals are used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficient high purity to permit its use without **lessening the accuracy of the determination.**

### 8.1 Reagents

**8.1.1 Reagent Water:** All reagent water is from Alpha's DI treatment system, and is demonstrated to be free of interferences or contaminants

**8.1.2 Solvents:** Hexane, methylene chloride (DCM), and acetone; pesticide grade or better. Store away from other solvents.

**8.2 Stock Standard Solutions:** All stock standard solutions are purchased from commercial vendors as ampulated certified solutions. When an ampulated stock solution is opened, it is transferred to a labeled vial. The expiration date of the stock solution is either the vendor specified expiration date, or 6 months from the date the ampule was opened, whichever is sooner. Stock solutions are stored per manufacturer's recommendations.

**8.2.1 For Samples undergoing fractionation**

**8.2.1.1 Aromatic Hydrocarbon Standard:** The Aromatic Hydrocarbon Standard consists of the 18 PAH compounds listed below, as well as one extraction surrogate and two fractionation surrogates.

| | |
|---|---|
| Naphthalene | Benzo(a)anthracene |
| 2-Methylnaphthalene | Chrysene |
| Acenaphthylene | Benzo(b)fluoranthene |
| Acenaphthene | Benzo(k)fluoranthene |
| Fluorene | Benzo(a)pyrene |
| Phenanthrene | Indeno(1,2,3-cd)pyrene |
| Anthracene | Dibenzo(a,h)Anthracene |
| Fluoranthene | Benzo(g,h,i)perylene |
| Pyrene | 1,2,3-Trimethylbenzene |
| 2-Fluorobiphenyl (fractionation surrogate) | 2-Bromonaphthalene (fractionation surrogate) |
| ortho-terphenyl (extraction surrogate) | |

**8.2.1.2 Aliphatic Hydrocarbon Standard:** The Aliphatic Hydrocarbon Standard consists of the 18 alkanes listed below, as well as one extraction surrogate, naphthalene, and 2-methyl-naphthalene.

| Compound | Carbon Number | Compound | Carbon Number |
|---|---|---|---|
| n-Nonane | $C_9$ | n-Tetracosane | $C_{24}$ |
| n-Decane | $C_{10}$ | n-Hexacosane | $C_{26}$ |
| n-Dodecane | $C_{12}$ | n-Octacosane | $C_{28}$ |
| n-Tetradecane | $C_{14}$ | n-Tricontane | $C_{30}$ |
| n-Hexadecane | $C_{16}$ | n-Dotriacontane | $C_{32}$ |
| n-Octadecane | $C_{18}$ | n-Tetratriacontane | $C_{34}$ |
| n-Eicosane | $C_{20}$ | n- Hexatriacontane | $C_{36}$ |
| n-Heneicosane | $C_{21}$ | n-Octatriacontane | $C_{38}$ |
| n-Docosane | $C_{22}$ | n-Tetracontane | $C_{40}$ |
| Naphthalene | - | 2-methyl-naphthalene | - |
| 1-chloro-octadecane (extraction surrogate ) | - | | |

**8.2.2 For Samples not undergoing fractionation**

**8.2.2.1 Aliphatic Hydrocarbon Standard:** The Aliphatic Hydrocarbon Standard for unfractionated samples consists of the 18 alkanes listed below, as well as two extraction surrogates, naphthalene, and 2-methyl-naphthalene.

| Compound | Carbon Number | Compound | Carbon Number |
|---|---|---|---|
| n-Nonane | $C_9$ | n-Tetracosane | $C_{24}$ |
| n-Decane | $C_{10}$ | n-Hexacosane | $C_{26}$ |
| n-Dodecane | $C_{12}$ | n-Octacosane | $C_{28}$ |
| n-Tetradecane | $C_{14}$ | n-Tricontane | $C_{30}$ |
| n-Hexadecane | $C_{16}$ | n-Dotriacontane | $C_{32}$ |
| n-Octadecane | $C_{18}$ | n-Tetratriacontane | $C_{34}$ |
| n-Eicosane | $C_{20}$ | n- Hexatriacontane | $C_{36}$ |
| n-Heneicosane | $C_{21}$ | n-Octatriacontane | $C_{38}$ |
| n-Docosane | $C_{22}$ | n-Tetracontane | $C_{40}$ |
| Naphthalene | - | 2-methyl-naphthalene | - |
| 1-chloro-octadecane | - | ortho-terphenyl | - |

**8.2.3 Extraction Surrogate Standards:** The extraction surrogates are 1-chloro-octadecane (COD) and ortho-terphenyl (OTP).

**8.2.4 Fractionation Surrogate Standards:** The fractionation surrogates are 2-Fluorobiphenyl and 2-Bromonaphthalene.

**8.2.5 Stock Standards**

1. Restek Custom NJEPH Aromatic Calibration Std, Cat # 30541, 2000 ug/ml
2. Restek Custom NJEPH Aliphatic Calibration Std, Cat# 30540, 2000 ug/ml
3. Restek 1-Chlorooctadecane Std, Cat#31098, 10,000 ug/ml
4. Restek O-Terphenyl Std, Cat#31097, 10,000 ug/ml
5. Restek MA Fractionation Surrogate Mix, Cat#31480, 4000 ug/ml
6. Restek Custom NJEPH Aromatic Frac Check Mix, Cat#564938, 400 ug/ml
7. Restek Custom NJEPH Aliphatic Frac Check Mix, Cat#564937, 400 ug/ml
8. Second Source- Absolute Standards NJEPH Aliphatic n-Hydrocarbons Part# 95708, 1000ug/mL
9. Second Source- Absolute Standards NJEPH Aromatic Hydrocarbons Part# 95709, 2000ug/mL

## 8.3 Calibration Standards

The Aliphatic calibration standards for both fractionated and unfractionated samples are prepared volumetrically by diluting the appropriate stock standard(s) with hexane. The Aromatic calibration standards for fractionated samples are prepared volumetrically by diluting the appropriate stock standard(s) with methylene chloride. Calibration standards expire 6 months from the date of preparation, or on the earliest expiration date of any of the stock solutions used to prepare the calibration standard. Calibrations are performed at the 5 concentration levels listed in Table 2. All working standards are stored refrigerated at 4 ±2 °C.

## 8.4 Surrogate Spiking Solution

The surrogate spiking solution is prepared at 100 ug/L in Acetone. This solution expires 6 months from the date of preparation or the expiration of the stock standard, whichever is sooner. Store refrigerated at 4 ±2 °C.

## 8.5 LCS/LCSD/MS Spiking Solution

A s second source is used from the Calibration Standards (Section 8.5.10 and 8.5.11) This solution is used for preparing Laboratory Control Samples (LCS), Laboratory Control Sample Duplicate (LCSD), Matrix Spikes (MS), and if requested, Matrix Spike Duplicates (MSDs) This solution is used for both fractionated and unfractionated samples. The concentration of the spiking solution is 100µg/mL. This solution expires 6 months from the date of preparation or the expiration of the stock standard, whichever is sooner. Store refrigerated at 4 ±2 °C. This solution must always be brought to room temperature prior to use.

## 8.6 Fractionation Surrogate Spiking Solution

This solution is added to all extracted samples and QC samples requiring fractionation prior to sample cleanup and fractionation using the silica gel cartridges. This serves as an important check on the ability of the fractionation to accurately separate the aliphatic from the aromatic compounds. The concentration of the surrogate solution is 100µg/mL. Solution expires 6 months from the date of preparation. Store refrigerated at 4 ± 2 °C.

## 8.7 Fractionation Check Solution

This solution is used to monitor the fractionation efficiency of the silica gel cartridge, and to establish the optimum volume of hexane needed to sufficiently elute aliphatic hydrocarbons from the cartridge without eluting the aromatic hydrocarbons prior to the methylene chloride elution. Fractionation checks are performed whenever a new lot of silica gel cartridges is received, prior to using them for actual samples.

To evaluate the fractionation check, both naphthalene and 2-methylnphthalene cannot exceed the breakthrough criteria of 5% in both the aliphatic and aromatic fractionsfor total concentration and the fractionation surrogates need to be within acceptable criteria.

The concentration of the solution is 200µg/mL. It contains all compounds from sections 8.2.1. Solution expires 6 months from the date of preparation. Store refrigerated at 4 ± 2°C.

Every new lot of Silca Gel needs to pass four consecutive checks. Without optimizing either the Hexane or Methylene Chloride volumes, the potential for breakthrough exits. The mean measured concentration of the individual fractionation compounds should be determined.

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.

### 8.8 Hydrogen gas: Ultra high purity.

### 8.9 Zero Air: From Alpha generator.

# 9. Quality Control

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

## 9.1 Blank

#### 9.1.1 Instrument Blank

Each day before calibration the analyst shall analyze a reagent blank to demonstrate that interference 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.

The instrument blank is also used for blank subtraction data within the 24 hour analytical window, if baseline subtraction is being used.

#### 9.1.2 Method Blank

Method blanks are performed with each extraction batch of 20 or less samples, according to the extraction SOPs. The extraction blank must not contain any of the individual target analytes or hydrocarbon ranges above the reporting limits. If any reportable analytes are detected in the blank, the entire extraction batch is suspect and re-extraction of all associated samples is required. The surrogate recoveries must also be within the acceptance criteria listed in Section 9.7. If surrogate acceptance criteria are exceeded, the extraction batch must be evaluated to determine if re-extraction or re-analysis is necessary.

Corrective Actions: If blank levels for any component are above 5x MDL and the sample concentrations present in the samples are greater than 10x blank level 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 10 X the blank level, the affected samples are re-extracted and reanalyzed. If a sample cannot be re-extracted or re-analyzed, the data is qualified as such. Samples must not be blank corrected.

#### 9.1.3 Solvent Blank

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.

## 9.2 Laboratory Control Sample (LCS)/ Laboratory Control Sample (LCSD)

**9.2.1** An LCS is extracted with each analytical batch of 20 samples or less. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS standard must be from a different source than that used for the initial calibration. The LCS is spiked with the aliphatic and aromatic compounds, as described in Section 8.5. The recovery of each of the compounds and ranges must be between 40% and 140%. Lower recoveries for nonane are permissible but must be greater than 25% and must be noted in case narrative.

**9.2.1.1 For an LCS undergoing fractionation,** If any recovery criteria are not met, the extract may be re-fractionated to see if the recoveries improve. If the criteria are still not met, the entire batch must be re-extracted. If this is not possible, due to insufficient sample or holding time exceedence, the analyst must submit the failure on a narrative sheet for inclusion in the client report.

**9.2.2** An LCSD is extracted with each analytical batch of 20 samples or less. The LCSD is separately prepared, processed and analyzed in the same manner as the LCS and is used as the data quality indicator of precision. The recovery of each of the compounds and ranges must be between 40% and 140%. Lower recoveries for nonane are permissible but must be greater than 25% and must be noted in case narrative.

**9.2.2.1 For and LCSD undergoing fractionation:**
If any recovery criteria are not met, the extract may be re-fractionated to see if the recoveries improve. If the criteria are still not met, the entire batch must be re-extracted. If this is not possible, due to insufficient sample or holding time exceedence, the analyst must submit the failure on a narrative sheet for inclusion in the client report.

**9.2.3** Breakthrough of naphthalene and 2-methylnaphthalene in the aliphatic fraction is calculated in both the LCS and LCSD. If breakthrough is > 5% in the LCS or LCSD, fractionation must be repeated on all stored affected extracts. 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. Breakthough is calculated by summing the concentration of naphthalene in both the aliphatic and aromatic protoins of the LCS or LCSD. This sum is then divided by the total amount of naphthalene in the aliphatic portion, and mutiplying by 100. (This calculation is also used to determine the breakthough of 2-methyl-naphthalene).

Example of Naphthalene % Breakthrough Calculation
Naphthalene in aromatic fraction = 50
Naphthalene in aliphatic fraction = 1.5
Total Naphthalene concentration = 51.5
% Naphthalene Breakthrough = $(1.5 / 51.5) \times 100$ = 2.9%

**9.2.3.1 For and LCS and LCSD not undergoing fractionation:**

An LCS and LCSD is extracted with each analytical batch of 20 samples or less. The LCS/LCSD consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS/LCSD standard must be from a different source than that used for the initial calibration. The LCS/LCSD is spiked with the aliphatic and aromatic compounds, as described in Section 8.5. The recovery of each of the compounds and ranges must be between 40% and 140%. Lower recoveries for nonane are permissible but must be greater than 25% and must be noted in case narrative. If the criteria are not met, the entire batch must be re-extracted. If this is not possible, due to insufficient sample or holding time exceedence, the analyst must submit the failure on a narrative sheet for inclusion in the client report.

Because the LCS/LCSD pair are not fractionated, the Aliphatic and Aromatic Compounds will be present together in the same extract. Due to instrument parameters, various alkanes can co-elute with PAH's when analyzed. Since each instrument is slightly different, some alkanes will be narrated as co-eluting with PAH's.

**9.2.4** The Analytical Batch Precision is determined from the Relative Percent Difference (RPD) of the concentrations (not recoveries) of LCS/LCSD pair. The RPD for the aliphatic and aromatic carbon range concentrations must be $\leq$ 25%. The FID retention times of the surrogates must match the previous calibration as described in previous section.

## 9.3 Initial Calibration Verification (ICV)

See Section 10.2

## 9.4 Continuing Calibration Verification (CCV)

See Section 10.4

## 9.5 Matrix Spike

A Matrix Spike is preformed a minimum of five percent or one per batch, which ever is more frequent. The MS(/MSD) is an aliquot of actual sample spiked with the aliphatic and aromatic compounds, as described in Section 8.5. The recoveries in the MS(/MSD), corrected for the concentrations found in the neat sample, must be between 40% and 140%. If a MS/MSD is performed, the %RPD should be less than 50%.

## 9.6 Laboratory Duplicate

A Sample Duplicate is preformed a minimum of five percent or one per batch, which ever is more frequent. The duplicate is a sample aliquot split from the same container as the sample, and is extracted and analyzed separately following the same procedures. The RPDs for any hits in the samples or for hydrocarbon ranges should be less than 50%.

## 9.7 Method-specific Quality Control Samples

### 9.7.1 Surrogates- For samples undergoing fractionation

All extracted samples and associated QC are spiked with the extraction surrogates listed in Section 8.3. Sample extractsare also spiked with the fractionation surrogates listed in Section 8.4 prior to cleanup and fractionation using the silica gel cartridges. All surrogate recoveries must be between 40% and 140%.

If any surrogatesfail the recovery criteria, samples may be re-fractionated and re-analyzed. If the surrogate limits are still not met, the affected samples must be re-extracted to confirm that the failure was due to sample matrix. If matrix effect is confirmed, this must be noted on a narrative sheet for inclusion in the client report; both sets of data are reported.

An exception to this is when large amounts of extracted material co-elute with any of the surrogate compounds, resulting in false high recoveries. When this is evident by examination of the sample chromatogram, re-extraction or re-fractionation is not required. Note the cause for the high recovery on a narrative sheet for inclusion in the client report.

### 9.7.2 Surrogates- For unfractionated samples

All extracted samples and associated QC are spiked with the extraction surrogates listed in Section 8.3. All surrogate recoveries must be between 40% and 140%.

If the surrogate limits are not met, the affected samples must be re-extracted to confirm that the failure was due to sample matrix. If matrix effect is confirmed, this must be noted on a narrative sheet for inclusion in the client report; both sets of data are reported.

An exception to this is when large amounts of extracted material co-elute with any of the surrogate compounds, resulting in false high recoveries. When this is evident by examination of the sample chromatogram, re-extraction or re-fractionation is not required. Note the cause for the high recovery on a narrative sheet for inclusion in the client report.

## 9.8 Method Sequence

The typical daily analytical sequence is:

- Instrument Blank
- Analytical Batch Opening Initial Calibration or mid range Continuing Calibration (REQUIRED)
- Laboratory Method Blank (REQUIRED)
- Laboratory Control Sample (REQUIRED)
- Laboratory Control Sample Duplicate (REQUIRED)
- 20 or less samples
- Matrix Spike (REQUIRED)
- Matrix Spike Duplicate (as requested)
- Closing mid-range continuing calibration standard after 20 samples (This standard may also be used as the analytical batch opening Continuing Calibration for the next analytical batch if batches are processed continuously.) (REQUIRED)

# 10. Procedure

## 10.1 Equipment Set-up

### 10.1.1 Sample Extraction

Aqueous samples are extracted at acid pH (less than pH 2) with methylene chloride using a separatory funnel (Method 3510C). See extraction SOP for details.

Solid samples are extracted with methylene chloride using Soxhlet extraction (Method 3540C) or Microwave extraction (Method 3546) See appropriate extraction SOP for details.

### 10.1.2 Extract Fractionation

Silica gel fractionation is used for sample cleanup and separation into aliphatic and aromatic extracts. Silica gel cartridges are purchased from commercial vendors, and tested prior to use . See appropriate extraction SOP for details.

### 10.1.3 GC Conditions

A dual-injector/dual-column/dual-detector approach involves the use of the columns listed in section 7.3. This allows for the simultaneous analysis of both fractions. Typical GC conditions are listed below, but may be altered as long as method performance criteria are met.

- Temperature 1: 60 $^{o}$C
- Time 1: 1 minute
- Ramp 1: 8$^{o}$C/minute
- Final Temperature 1: 290 $^{o}$C
- Final Time 1: 18.25 minutes
- Total Time: 48 minutes
- Injector temperature: 285 $^{o}$C
- FID temperature: 315 $^{o}$C
- Carrier gas: Helium
- Carrier pressure program: 5.2 psi initial
- Detector Air: 250 mL/minute
- Detector Hydrogen: 40 mL/minute
- Injection volume: 1 µL

## 10.2 Initial Calibration

**10.2.1** Prepare calibration standards using the procedures in Section 8.3 at the concentrations listed in Table 2. The calibration standards are aliquoted into autosampler vials and capped prior to loading onto the autosampler tray.

**10.2.2** Establish the GC operating conditions by loading the appropriate GC method. Typical instrument conditions are listed in .Section 10.1.3. The same operating conditions are used for calibrations and sample analyses. Create the analytical sequence using the Chemstation data acquisition software.

**10.2.3** A 1µL injection volume of each calibration standard is typically used. Other injection volumes may be employed, provided that the analyst can demonstrate adequate sensitivity for the compounds of interest. The same injection volume must be used for calibration standards, samples and QC samples.

**10.2.4 Calibration Factors**

**10.2.4.1 Individual PAH Target Compounds**: In each standard, calculate the calibration factor for each analyte, the mean calibration factor, and the relative standard deviation (RSD) of the calibration factors, using the Target data processing software. The calculations are performed automatically, using the formulae listed in Alpha's Quality Manual and the CF equation below:

Calibration factor: Target PAH Analytes:

$$\textit{Calibration Factor (CF)} = \frac{\textbf{area of peak}}{\textbf{concentration injected (ng/µL)}}$$

**10.2.4.2 Hydrocarbon Ranges**: In each standard, calculate the calibration factor for each range, the mean calibration factor, and the relative standard deviation (RSD) of the calibration factors, using the Target data processing software. The calculations are performed automatically, using the formulae listed in Alpha's Quality Manual.

Range Calibration Factor: Hydrocarbon Ranges:

$$\textit{Range CF} = \frac{\textbf{Area of Summation of Range Components}}{\textbf{Total concentration injected (ng/µL)}}$$

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-methylnaphthene in the aliphatic fraction must be subtracted out from the appropriate carbon range.

**10.2.5 Initial Calibration Acceptance Criteria**

For samples not requiring fractionation: Only an Aliphatic ICAL is injected containing the compounds listed in 8.2.2

If the RSD for an analyte or range is $\leq$ 25%, then the response of the instrument for this compound is considered linear over the range and the mean calibration factor can be used to quantitate sample results. If the RSD for any analyte is >

25%, then linearity through the origin cannot be assumed. The calibration must be repeated for any compounds that fail, or a calibration curve may be generated for this compound and used for sample quantitation instead of the mean calibration factor. If a linear regression curve is used, the correlation coefficient I must be at least 0.99.

For samples requiring fractionation: Both an Aliphatic and Aromatic ICAL is injected containing the compounds listed in 8.2.1.

If the RSD for an analyte or range is ≤ 25%, then the response of the instrument for this compound is considered linear over the range and the mean calibration factor can be used to quantitate sample results. If the RSD for any analyte is > 25%, then linearity through the origin cannot be assumed. The calibration must be repeated for any compounds that fail, or a calibration curve may be generated for this compound and used for sample quantitation instead of the mean calibration factor. If a linear regression curve is used, the correlation coefficient I must be at least 0.99.

**10.2.5.1 Mass Discrimination Check**
The mass discrimination in each ICAL level is checked before performing any -sample analyses. The response ratio of C30/C20 must be ≥ 0.8. If less than 0.8, the column should be repositioned until the mass discrimination is minimized.

**10.2.5.2** EPH retention time (Rt) windows are defined as beginning 0.1 minutes before the Rt of the beginning marker compound and ending 0.1 minutes after the Rt of the ending marker compound.

EPH marker compounds and windows are summarized in Table 4.

**10.2.5.3** If a TPH analysis is performed without fractionation, TPH retention time (Rt) windows are defined as beginning 0.1 minutes before the Rt of n-Nonane and ending 0.1 minutes after the Rt of n-Tetracontane.

## 10.3 Equipment Operation and Sample Processing

**10.3.1** Inject 1uL-of extract using an autosampler device.

**10.3.2 Instrument Performance**

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

**10.3.2.2** 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.

**10.3.2.3** Monitor the retention time for each surrogate using data generated from calibration standards. Major shifts in retention time for surogates should be monitored and not exceed 0.1 min. If retention time shift occurs, locate the source of the problem.

**10.3.3 Concentration of Petroleum Hyrdocarbons**

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 unresolved "envelope." This total area must be adjusted to remove area response of the solvent, surrogates and GC column bleed.

**10.3.4 Establishing the Baseline**

**10.3.4.1** 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 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 peak area integration for the fractional ranges must be from baseline (ie. must include the unresolved complex mixture "hump" area). However, the unresolved "hump" areas are not to be included in the integration of individual compounds such as surrogates.

**10.3.4.2** 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 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.

**10.3.4.3** If baseline correction is used, then the baseline must be reestablished for every analytical batch by the analysis of a system solvent blank.

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

## 10.4 Continuing Calibration

**10.4.1** The initial calibration curve is verified on each working day prior to the analysis of samples by the injection of the Level 3 Calibration Standard. The calibration standard is a mid-range standard prepared from the same stock standard solution used to develop the calibration curve. Continuing calibration standards should be run throughout the analytical sequence after every 10 samples, but at a minimum frequency of 20 samples, or 24-hours. Each analytical sequence must end with a calibration standard.

**10.4.1.1 For samples not undergoing fractionation,**

The percent difference (%D) for all aliphatic analytes must be<30%, and the %D for the Total EPH Range must be <25%. Any sample associated with a non-compliant opening or closing calibration standard must be re-analyzed.

**10.4.1.2 For fractionated samples-**

The percent difference (%D) for all aliphatic and aromatic analytes must be <30%, and the %D for the carbon ranges must be <25%. Any sample

associated with a non-compliant opening or closing calibration standard must be re-analyzed.

**10.4.1.3 Mass Discrimination Check**

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 must be $\geq$ 0.8. If less than 0.8, the column should be repositioned until the mass discrimination is minimize

**10.4.2** If the %D criteria cannot be met, inspect the gas chromatographic system to determine the cause and perform whatever maintenance is necessary before verifying calibration and proceeding with sample analysis.

**10.4.3** If after maintenance the system still fails the calibration verification criteria, a new initial calibration curve must be analyzed.

## 10.5 Preventive Maintenance

**10.5.1** Routine preventive maintenance must be performed to maintain GC system performance. This includes periodic replacement of injector septa, replacement of injector liner(s), and clipping several inches off of the injector end of the capillary column.

**10.5.2** Additional maintenance may be required if system performance degrades. Autosampler syringes and syringe needles must be periodically inspected, especially if erratic response or peak discrimination is seen. If the maintenance steps listed above do not improve system performance, it may be necessary to replace the GC column(s).

# 11. Data Evaluation, Calculations and Reporting

## 11.1 External Standard Calculations

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:

**11.1.1 Aqueous samples**

$$C = \frac{(A)\,(D)\,(V_e)}{CF(V_s)}$$

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

Where:

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

**11.1.2 Soils/Soilds/Sludge**

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

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

Where:

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

S = Dry sample weight, mg

**11.1.3 Total EPH Concentration =** Total of the 4 Aromatic carbon ranges and 4 Aliphatic carbon ranges

## 11.2 Data Report Format

Information regarding specific reporting requirements and deliverables may be found in section 12 of *Analysis of Extractable Petroleum Hydrocarbons (EPH) in Aqueous and Soil/Sediment/Sludge Matrices, New Jersey Department of Environmental Protection Site Remediation Program, Version 1.1, October 2009 Revision 2.*

# 12. Contingencies for Handling Out-of-Control Data or Unacceptable Data

Holding time exceedence, improper preservation and observed sample headspace are noted on the nonconformance report form.

Perform instrument maintenance as described throughout this SOP as needed when instrument calibration criteria are not met. Record all maintenance in the instrument maintenance logbook.

All batch and sample specific QC criteria outlined in Section 9 are evaluated by the analyst prior to approval of the data. When any QC criteria fail, the cause for the failure must be identified and corrected. This may include instrument recalibration followed by sample reanalysis or sample re-extraction. If it is determined that the failure is due to sample matrix effects, a project narrative report is written by the analyst for inclusion in the data report. If there is insufficient sample volume to perform the re-analysis for confirmation, this is also noted in the narrative and included in the client report.

# 13. Method Performance

## 13.1 Method Detection Limit Study (MDL) / Limit of Detection Study (LOD) / Limit of Quantitation (LOQ)

The laboratory follows the procedure to determine the MDL, LOD, and/or LOQ as outlined in Alpha SOP/08-05. These studies performed by the laboratory are maintained on file for review.

## 13.2 Demonstration of Capability Studies

The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method. Each time a method modification is made, the analyst is required to repeat the procedure.

To demonstrate initial laboratory capability, analyze a minimum of seven replicate reagent water and clean sand blanks spiked with each analyte of interest at approximately 100 µg/L and 10 mg/kg, respectively.

**13.2.1** Extract each replicate according to the extraction SOP, and analyze each replicate according to the procedures described in Section 10.3.

**13.2.2** Calculate the measured concentrations of each analyte in all replicates, the mean accuracy (as percentage of true value) for each analyte, and the precision (as %RSD) of the measurements for each analyte.

**13.2.2.1** For each analyte, the mean accuracy, expressed as a percentage of the true value, must be within ± 40% of the true value for both aqueous and soil matrices.

**13.2.2.2** The %RSD for each analyte must be ≤25%. A higher %RSD is allowed for n-Nonane.

**13.2.3** For each matrix, the FID retention times of the surrogates must match those in the calibration standard.

# 14. Pollution Prevention and Waste Management

Refer to Alpha's Chemical Hygiene Plan and Waste Management and Disposal SOP for further pollution prevention and waste management information.

# 15. Referenced Documents

Chemical Hygiene Plan

SOP/08-05 MDL/LOD/LOQ Generation

SOP/08-12 IDC/DOC Generation

SOP/14-01 Waste Management and Disposal SOP

# 16. Attachments

Table 1 – REPORTING LIMITS
Table 2 – LIST OF COMPOUNDS AND CALIBRATION LEVELS
Table 3 – HOLDING TIMES AND PRESERVATION REQUIREMENTS
Table 4 – EPH MARKER COMPOUNDS

**Table 1**
**Reporting Limits**

| Parameter | Aqueous | Soil |
|---|---|---|
| C9-C12 Aliphatic Hydrocarbons | 0.12 mg/L | 8.0 mg/Kg |
| C12-C16 Aliphatic Hydrocarbons | 0.08 mg/L | 5.33 mg/Kg |
| C16-C21 Aliphatic Hydrocarbons | 0.12 mg/L | 8.0 mg/Kg |
| C21-C40 Aliphatic Hydrocarbons | 0.40 mg/L | 26.67 mg/Kg |
| C10-C12 Aromatic Hydrocarbons | 0.08 mg/L | 5.33 mg/Kg |
| C12-C16 Aromatic Hydrocarbons | 0.12 mg/L | 8.0 mg/Kg |
| C16-C21 Aromatic Hydrocarbons | 0.20 mg/L | 13.33 mg/Kg |
| C21-C36 Aromatic Hydrocarbons | 0.32 mg/L | 21.33 mg/Kg |
| Total EPH | 1.44 mg/L | 95.99 mg/Kg |
| Total EPH (unfractionated) | | 24.0 mg/kg |

**Table 2**
**List of Compounds and Calibration Levels**

| Component | Concentration of standard analytes (µg/mL) | | | | |
|---|---|---|---|---|---|
| | Level 1 | Level 2 | Level 3 | Level 4 | Level 5 |
| Individual Aliphatic, Aromatic | 20 | 100 | 250 | 500 | 1000 |
| Total EPH (unfractionated) | 20 | 100 | 250 | 50 | 1000 |

**Table 3**
**Holding Times and Preservatives for EPH Samples**

| Matrix | Container | Preservation | Holding Time |
|---|---|---|---|
| Aqueous Samples | 1 Liter amber glass bottle with Teflon-lined screw cap | Add 5mL of 1:1 HCl; cool to 4 ±2°C | Samples must be extracted within 14 days and extracts analyzed within 40 days |
| Soil/Sediments Samples | 4 oz. (120mL) widemouth amber glass jar with Teflon-lined screw cap | Cool to 4 ±2°C | Samples must be extracted within 14 days and extracts analyzed within 40 days |

**Table 4**
**EPH Marker Compounds**

| Range/Hydrocarbon Standard | Beginning Marker Compound | Ending Marker Compound |
|---|---|---|
| $C_9$ – $C_{12}$ Aliphatic Hydrocarbons | n-Nonane | n-Dodecane |
| $C_{12}$ – $C_{16}$ Aliphatic Hydrocarbons | n-Dodecane + 0.1 min | n-Hexadecane |
| $C_{16}$ – $C_{21}$ Aliphatic Hydrocarbons | n-Hexadecane + 0.1 min | n-Heneicosane |
| $C_{21}$ – $C_{40}$ Aliphatic Hydrocarbons | n-Heneicosane + 0.1 min | n-Tetracontane |
| $C_{10}$ – $C_{12}$ Aromatic Hydrocarbons | 1,2,3-Trimethylbenzene | Naphthalene |
| $C_{12}$ – $C_{16}$ Aromatic Hydrocarbons | Naphthalene + 0.1 min | Acenaphthene |
| $C_{16}$ – $C_{21}$ Aromatic Hydrocarbons | Acenaphthene + 0.1 min | Pyrene |
| $C_{21}$ – $C_{36}$ Aromatic Hydrocarbons | Pyrene + 0.1 min | Benzo (g,h,i) Perylene + 1.0 min |
| Total EPH (for samples not requiring fractionation) | -0.1 min before n-Nonane | +0.1 after n-Tetracontane |

Note: The “0.1 min” are maximums. The laboratory should use less than the “compound + 0.1 min” as the carbon range marker if peak shape and chromatographic resolution are favorable