Standard Operating Procedure for:

Analysis of Petroleum-Range Organics by GC-FID (FL-PRO Method) and Analysis of Extractable Petroleum Hydrocarbons (EPH) by GC-FID (The Massachusetts Method)

DEPARTMENT OF ENVIRONMENTAL PROTECTION
CHEMISTRY SECTION
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1. SCOPE AND APPLICATION

1.1 This method describes the analysis of Petroleum-Range Organics (FL-PRO Method) and analysis of Extractable Petroleum Hydrocarbons (EPH) (The Massachusetts Method). Extracts from water, sediment and waste samples (DEP SOP SV-004) are analyzed by GC-FID for the LIMS test ID: W-FL-PRO, S-FL-PRO, WAS-FL-PRO, W-EPH and S-EPH.

1.2 In Florida Department of Environmental Protection's *Method for determination of Petroleum Range Organics* (FL-PRO), the concentration of Petroleum Hydrocarbons of range C_8-C_{40} (normally gasoline through motor oil) is measured in water, soil/sediment and waste samples using Gas Chromatography with Flame Ionization Detection (GC-FID).

1.3 Petroleum Hydrocarbons: All chromatographic peaks, both resolved and unresolved, eluting between the peak start of n-octane (n-C_8) and the peak end after n-tetracontane (n-C_{40}). Quantitation is based on direct comparison of the area within this range to the total area of the Petroleum Hydrocarbon standard as determined from FID response using baseline - baseline integration.

1.4 Petroleum Hydrocarbon Standard: A 17-component mix of all even - numbered normal alkanes from C_8 to C_{40} (Table 1). This standard serves as a quantitation standard and a retention time window defining Petroleum Hydrocarbons. Other organic compounds, including chlorinated hydrocarbons, phenols, phthalate esters as well as biodiesel fuels are also measurable. As defined in the method, the Petroleum Range Organics method results include these compounds. Biodiesel fuels will typically elute shortly after the o-terphenyl surrogate, as a cluster of several sharp peaks. Animal and vegetable oil and grease may also be partially measurable if the sample is not cleaned up before analysis, and the method prescribed integration window is applied. In those cases the peaks that would typically elute in the C8 to C40 range are usually some minor impurities or decomposition products. Animal fats and vegetable oils are mixtures of fatty acid triglycerides, which have much higher boiling points than the TRPH range. They can only be eluted when using high temperature GC columns and injector/column temperatures as high as 380C. In order to eliminate false positives from these sources, **the silica cleanup (9.1.6) is a mandatory part of this procedure**. However one needs to always consider the possibility that large concentrations of fats and oils may overwhelm the silica cleanup cartridge and still make it into the final extract. A variety of biogenic materials may also be extracted by the procedure. That includes various terpenes as well as plant oils and waxes that are often present in vegetation rich soils. Other natural organics that may be measured are long chain carboxylic acids (fatty acids), and steroids such as cholesterol. Lastly, not all petroleum range hydrocarbons always originate from petroleum products. Some background levels of various hydrocarbons are to be expected in certain organic rich formations like peat moss or other accumulations of partially decayed vegetation.

1.5 Petroleum Source / Petroleum Products Identification Standards: Various commercial petroleum products are used to qualitatively identify petroleum product types in the samples by direct visual comparison of chromatographic profiles. These standards may be purchased from vendors or obtained from commercial sources (a few of those are listed in Table 1). If the sample is suspected to be a crude oil, the sample can be further analyzed, if necessary, by GC/MS analysis. Direct visual comparison of extracted ion chromatograms of reference oils or a known crude oil source may be compared to the spilled oil sample in GC/MS analysis (refer to DEP SOP SV-006).

1.6 In Massachusetts Department of Environmental Protection's Method for Determination of Extractable Petroleum Hydrocarbons (EPH), the collective concentrations of extractable aliphatic (C_9 through C_{36}) and aromatic (C_{11} through C_{22}) petroleum hydrocarbons is measured in water and sediment using Gas Chromatography with Flame Ionization Detection (GC-FID). Petroleum products suitable for analysis by this method include kerosene, jet fuel, diesel fuel, certain lubricating oils, and fuel oils #2 through #6. Products with a significant percentage of hydrocarbons outside of this range (lighter than C_9 or heavier than C_{36}) such as gasoline, mineral spirits, petroleum naphtha's, or heavy lubricating oils are not suitable for this analysis.

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2. SUMMARY OF THE METHOD

2.1 For FL-PRO, one liter of water or 25 g of sediment or 1 g of waste sample is spiked with two surrogates, extracted with methylene chloride, and concentrated to 2 mL final volume. Half of the extract is cleaned up with silica gel to remove potential organic interference. A 1 µL aliquot of the final extract is injected onto a capillary gas chromatography instrument equipped with a flame ionization detector (GC-FID). Quantitation of the sample extracts is based on the detector response compared to a series of normal alkane standards, using a baseline-to-baseline integration over the C_8 to C_{40} compound range.

2.2 For EPH, one liter of water or 10 g of sediment is extracted with methylene chloride and concentrated to 2 mL in hexane. Half of the extract is fractionated with 5 g silica gel into an aliphatic fraction and an aromatic fraction. A 1-µL aliquot of the final extract is injected into a capillary gas chromatography instrument equipped with a flame ionization detector (GC-FID). Quantitation of the sample extracts is based on the detector response compared to a series of normal alkane standards, using a baseline to baseline integration over the C_9 through C_{36} compound range and C_{11} through C_{22} aromatic hydrocarbon standards using baseline to baseline integration.

3. APPARATUS AND EQUIPMENT

3.1 Bottles -- 25 mL, amber glass with Teflon-lined screw caps.

3.2 Auto sampler vials -- 2 mL, with Teflon-lined septa top, to fit the Agilent 7683 auto sampler.

3.3 GC-FID system: Gas chromatography, Agilent 6890N Network GC System equipped with a 7683 Series Injector.

GC-FID Operating Conditions: (this serves as guideline only, different instrument may have different settings) for both FL-PRO and EPH methods

Parameter	Setting
Signal 1:	A: 11.8; Range: 2; Zero: 0.0; ATTN: 0
Analytical Column (6890N/MSD/FID1/2):	Phenomenex - ZB-5 30 m x 0.25 mm x 0.25 µm (or equivalent)
GC Oven Temperature Program:	50 °C for 3 min., to 320 °C at 22 °C /min. and hold for 14.73 min. Run Time = 30 min.
Inlet:	Temp: 275 °C; Mode: Splitless; Pressure: Constant Flow ON, 17.15 psi at 50 °C (1.6 mL/min); Purge Time ON: 2.0 min. Purge Flow: 50 mL/min. Purge Time OFF: 0.0 min. Injection Volume: 1 µL; Total Flow: 53.8 mL/min. Septum Purge: 2.0 mL/min. Gas saver: ON, Saver Flow: 25 mL/min.
Detector:	Temp: 250 °C; H2 at 40 mL/min., Air at 450 mL/min. & Aux Gas at 45 mL/min.
Signal 1:	Data Rate: 20Hz, Range: 0; Zero: 0.0; ATTN: 0, Partial Data.

3.4 Helium, UPC grade, is the carrier gas in the gas chromatographs. The helium must be passed through an oxygen filter before entering the gas chromatographs.

3.5 Data system: A computer with chromatographic data system must be interfaced with the chromatographic detector. The chromatographic data system must allow continuous acquisition and storage of all chromatographic data obtained throughout the run sequence, and subsequent data processing. Agilent 6890N GC/FID is controlled by the Chemstation software software and the data is processed (after conversion) by the Masshunter software (GC version).

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4. REAGENTS AND CHEMICALS

NOTE: Record Lot Numbers of all the reagents and solvents used in the Note Book

4.1 Solvent: methylene chloride (optima grade), carbon disulfide (spectra-analyzed), and acetone (HPLC grade).

4.2 Stock Standard Preparations: Primary and secondary stock standards are available in pre-made mixtures.

4.3 FL-PRO Standard Preparation, see DEP SOP SV-009 for details of preparation.

4.4 EPH Standard Preparation, see DEP SOP SV-009 for details of preparation.

5. SAMPLE PREPARATION PROCEDURE

5.1 Refer to TRPH Extraction SOP SV-004.

5.2 All extracts must be analyzed within 40 days of extraction.

6. SAMPLE ANALYSIS/QUANTITATION

6.1 **Initial Calibration for FL-PRO**: Calibration standards are prepared at following concentration levels: 170, 425, 850, 1700, 2550, 3400, 5100 ug/mL for TRPH and corresponding individual surrogate concentrations of 10, 25, 50 ,100, 150, 200, 300 ug/mL. freshly prepared calibration standards are given six months expiration date. The external standard calibration technique is used for quantifying TRPH. The standard deviation for the response of the calibration standards must be within 20 % to insure that the standard concentrations are within the linear range of the calibration curve. If the average response factor cannot be used then a linear regression shall be calculated. The correlation coefficient shall be equal or greater than 0.995. To use a quadratic fit a minimum of six calibration levels is required. In all cases, response of the standards must be determined by continuous integration of all responses (**excluding surrogates**) from a forced baseline beginning at a point prior to the elution of the compound C_8 to a point beyond the compound C_{40}. **The selection of the time interval should be based on injection of appropriated pattern recognition standards and must be constant for all standards and samples.**

6.2 **Calibration Factor for FL-PRO**: Determine the area response of the 17 hydrocarbon components and calculate the calibration factor for each level as the ratio of area of standard mix against the mass injected:

$$\text{Calibration Factor} = \frac{\text{Total PHS Area}}{\text{Total PHS mass injected (ng)}}$$

PHS: Petroleum Hydrocarbon Standard

PHS Area: Response as integrated in 6.1.

Total PHS: Refers to the sum of the concentration of the individual components as defined in DEP SOP SV-009, section 5.9.3.

6.3 **Initial Calibration for EPH**: The internal standard calibration technique is used for quantifying EPH. The standard deviation for the response of the calibration standards must be within 25 % to insure that the standard concentrations are within the linear range of the calibration curve. The

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integrated area for each individual component peak (including surrogates) eluting from n-Nonane through n-Hexatriacontane shall be determined using a valley-to-valley integration baseline.

6.4 **Response Factor for EPH**: The integrated area for each component peak (including surrogates) eluting from n-Nonane through n-Hexatriacontane shall be determined using a valley-to-valley integration baseline. Determine the area response for each of the hydrocarbon components and calculate the response factor (RF) for each level:

$$\text{Response Factor} = \frac{(\text{Area of component peak}) \times (\text{I.S. concentration in } \mu g/mL)}{(\text{Concentration of component in } \mu g/mL) \times (\text{I.S. peak area})}$$

If the percent relative standard deviation (%RSD) of the 5 response factors is less than or equal to 25%, then the average RF for that component can be used for calculations. Alternatively, the RF results can be used to construct a response ratio (Ax/Ai.s.) vs. concentration ratio (Cx/Ci.s.) calibration curve.

6.5 **Range Response Factor for EPH**: Range One Aliphatics begin at a point immediately prior to the elution of C_9 to a point just before C_{19}. Range Two Aliphatics begin at this same point just before C_{19} to a point just beyond C_{36}. The Aromatic Range (C_{11} through C_{22}) is from a point just before Naphthalene to a point just beyond Benzo (g, h, i) perylene. If Total Petroleum Hydrocarbons (TPH) is done without fractionation, the retention times (Tr) are just before C_9 and just after C_{36}.

A collective response factor must also be determined for each hydrocarbon range of interest. To calculate the collective RFs for a given range, tabulate the summation of peak areas of all components against the total concentration injected, using a forced baseline projection, and subtracting the surrogate and I.S. areas:

$$\text{Range RF} = \frac{(\text{Range area - Surrogate and I.S. areas}) \times (\text{Concentration of I.S.})}{(\text{Area of I.S.}) \times (\text{Concentration of range peaks})}$$

If the percent relative standard deviation (%RSD) of the 5 range response factors is less than or equal to 25%, then the average RF for that range can be used for calculations.

6.6 **Initial and Continuing Calibration Verification**: The accuracy of the initial calibration must be verified by injecting a midpoint concentration standard (Initial Calibration Verification, ICV) solution that was obtained from a different source (different vendor). The calculated value shall be within +- 20% of expected value. Additionally, the working calibration factor or calibration curve must be verified on each working day before the analysis started (if the calibration curve is not established on the day) by the injection of a continuing calibration verification standard (CCV) at 40µg/mL individual, 680 ug/mL total TRPH concentration). This standard must be evaluated prior to the analysis of any samples.

6.6.1 If the response for this standard varies from the predicted response be more than ± 25%, a new initial calibration curve must be prepared and verified before samples are analyzed.

$$\text{Percent Difference} = \frac{(R_1 - R_2)}{R_1} \times 100$$

R_1: Average CF from the initial calibration curve or standard response from initial calibration curve

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R_2: Calibration Factor from CCV or standard response from CCV

In addition, a calibration check standard (CCV) must be analyzed every 10 samples or less and at the end of each analysis sequence. Evaluate the continuing calibration response. If the performance criteria fail, then the instrument must be recalibrated and all of the samples injected after the failed check sample must be reanalyzed.

6.6.2 The retention time window for the surrogates and the compounds C_8 and C_{40} shall be within the established range. If they are out of the acceptance range, then a new initial calibration must be prepared and verified before samples are analyzed. Usually, after maintenance (e.g. cutting the injector end column, cleaning or changing detector jet) the retention times and sensitivity will change and will require that a new initial calibration curve be prepared.

6.7 Samples are analyzed by GC/FID using conditions established in 3.3. For EPH additional confirmation of analytes can be made using GC/MS. Suggested major ions are listed in tables one and two at the end of this SOP.

6.8 A methylene chloride blank (for aromatics and FL-PRO) and a hexane blank (for Aliphatics) must be analyzed at the beginning of every analysis sequence to determine the area generated from normal background under the conditions used. The calculated concentration should be 5 times less than the MDL. Baseline subtraction is not necessary and is not recommended.

6.9 Qualitative Identification (Pattern Recognition): The laboratory may qualitatively identify the petroleum products when reporting data by direct comparison of sample chromatograms to retention times and peak patterns of known petroleum standards or a petroleum source. The experience of the analyst weighs heavily in the interpretation of the chromatogram. Because of weathering, the patterns may not be a perfect match; however, the characteristics of a petroleum hydrocarbon pattern must be present. Environmental samples may contain more than one type of product, and loss of light-end components may mean the product has been in the subsurface a longer period of time. Qualitative information may be reported on the final laboratory report. This information should include an alkane range. If possible, product identification should be included and may be based on the individual laboratory's chromatograms of commercial petroleum products (e.g., diesel fuel, motor oil, etc.). If the sample is suspected to be a crude oil, the sample can be further analyzed, if necessary, by GC/MS analysis. Direct visual comparison of extracted ion chromatograms of reference oils or a known crude oil source may be compared to the spilled oil sample in GC/MS analysis (refer to DEP SOP SV-006).

7. RESULTS CALCULATIONS:

7.1 The integrated area for each component peak (including surrogates) eluting from n-Nonane through n-Hexatriacontane in EPH and from n-octane through n-tetracontane in FL-PRO shall be determined using a valley-to-valley integration baseline.

7.2 Calibration factor for FL-PRO:

$$Cs = \frac{(Ax)\,(Ve)\,(D)}{(CF)\,(Inj)\,(Vs)}$$

Where:

Cs = Concentration of Petroleum Hydrocarbons (mg/L or mg/kg)

Ax = Response for the Petroleum Hydrocarbons in the sample (baseline to baseline integration subtracting the area of surrogates), units in area

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Ve = Volume of final extract (mL)

D = Dilution factor, if dilution was performed on the sample prior to analysis. If no dilution was made, D = 1, dimensionless

CF = Average Calibration Factor from initial calibration (See 6.2)

Inj = Volume of injected sample (µL)

Vs = Volume of sample extracted in ml or weight of sample in grams

7.3 Individual and Range Concentration for EPH:

The integrated area for each range (including surrogates) shall be determined using a forced baseline integration technique.

$$Cx = \frac{(Rx)(Ve)(D)\ (Conv)}{(RF)(Vs)}$$

Where:

Cx = Concentration of Petroleum Hydrocarbon (mg/L or mg/kg)

Rx = Area response for the component times the Internal Standard concentration divided by the Internal Standard area response (units are µg/mL). TARGET automatically calculates and prints out the Rx on the report.

Ve = Effective volume of final extract (mL). Due to only half of the extract being used to generate a 1 mL analysis sample, Ve is usually equal to two.

D = Dilution factor, if dilution was performed on the sample prior to analysis. If no dilution was made, D = 1, dimensionless.

Conv = conversion factor of mg/1000µg

RF = Average Response Factor from initial calibration (See 6.2)

Vs = Volume of sample extracted in liters or dry weight of sample in kilograms.

7.4 Dry weight determination:

$$\text{mg/dry kg PH} = \frac{Cs}{1 - (\%\text{moisture}/100)}$$

Where:

Cs = Concentration of Petroleum Hydrocarbons (mg/L or mg/kg)

7.5 Calculation of recoveries (FL-PRO):

7.5.1 The surrogate, Lab Fortified Blank and Matrix spikes recoveries in each sample must be calculated. The peak areas obtained should be based on a valley-to-valley integration.

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7.5.2 If the surrogate recovery is outside of established limits, then the results must be flagged and an explanation offered. If any of the above surrogate falls outside control limits, re-extract the effected sample with proper QC even after expiration and follow DEP SOP LB-027 for reporting.

Compound & Matrix	Acceptance limits %
Ortho-Terphenyl - Water	82-142
Nonatriacontane_Water	42-193
Ortho-Terphenyl_Soil/Waste	62- 109
Nonatriacontane_Soil/Waste	60-118

7.5.3 Check the Lab Fortified Blank recoveries and matrix spikes recoveries, and they must be within the acceptance range and the range is set by the method.

Compound & Matrix	% Rec	RPD
TRPH_LFB_Water	55 - 118	< 20
TRPH_LFB_Soil	62 - 153	< 25
TRPH_MS_Water	41-101	< 20
TRPH_MS_Soil	62-204	< 25

7.5.4 A comment must be added to the qualified data in the final report explaining any deviation from the routine limits whenever the spikes or surrogates are out of range (DEP SOP LB-027).

7.5.5 Check the method blank for any interfering contaminants. The MDLs may have to be elevated if the blank(s) indicate contamination.

8. REPORTING AND DOCUMENTATION

8.1 When analysis is complete, the QC Manager is used to download the final sample results into the Laboratory Information Management System (LIMS). If a sample has been diluted then make sure that the information was entered properly into the QC Manager.

8.2 Add the appropriate qualifiers and comments to the sample data in the QC Manager after performing a complete review of the sample data and QC data. Follow DEP SOP SV-011, BNA Group Data Review/Authorization Checklist for details of data review and reporting, and Section 11 (QUALITY CONTROL). See DEP SOP LB-027, Standard Operating Procedure for Reporting Qualified Data for guidelines for qualifying data when quality control results are outside established control limits and re-analysis is not a viable or desired option.

8.3 Definitions of the available qualifying codes are listed in DEP SOP LB-027

8.4 All quantitation reports for samples and QC should be placed in a results folder labeled with the job number, the sample numbers, and the type of analysis.

8.5 Retrieve the field folders (containing the field sheets) and check the data against the field sheets to see if it makes sense (i.e., does the equipment blank contain several hits while an effluent sample does not?) If anything looks suspicious, further research is necessary before posting results.

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8.6 Enter the results for each sample in the analysis results form. Print out QC results from the QC Manager. Include a copy of dilutions page if any. Also include a print out of sample positives from the data review and file it in the data folder.

8.7 Submit the result folder to the GC group section supervisor. The supervisor will review results and then authorize the sample. The supervisor will then file the folders in the GC group lab.

9. DATA ARCHIVAL

9.1 For the GC-AGILENT-FID system:

9.1.1 Move the data files soon after collection from the hard disk of the instrument computers to the network drive \\FLDEP1\dear\labs\lab3\chemdata\organic\GC\BACKUP_GC-AGILENT-FID Raw data files on the hard disk of each instrument may be deleted after 3 to 4 months or they are no longer in need.

9.1.2 Copy the Masshunter upload file into \\FLDEP1\dear\labs\lab3\chemdata\organic \GC\UPLOAD_GC-AGILENT-FID to convert in QC Manager for reporting in LIMS.

9.1.3 The archived data may be retrieved by making a request to the data group or the GC supervisor. Make sure when setting up an injection sequence to write down the name of the data files with the associated sample information in the injection log

10. QUALITY CONTROL

10.1 See BNA SOP SV-010, Quality Assurance/Quality Control in the Semi-Volatile Organics Laboratory (BNA-GC/MS) for detailed information on quality control, definitions and interferences. See DEP SOP LB-027, Standard Operating Procedure for Reporting Qualified Data for guidelines for qualifying data when quality control results are outside established control limits and re-analysis is not a viable or desired option.

11. SAFETY/HAZARDOUS WASTE MANAGEMENT

11.1 The toxicity and carcinogenicity of each reagent used in this method has not been precisely defined. All of the chemicals used in this method should be treated as a potential health hazard. Please review the relevant Material Safety Data Sheets.

11.2 Wear gloves and safety glasses at all times when working with standards. The lower petroleum range compounds and solvents are particularly volatile and must be handled in a hood. Carbon disulfide has a very unpleasant odor. Use care when handling all standards and solvents.

11.3 Please refer to the safety SOP OG-001, Safety and Waste Management Practices in the Organic Analysis Groups (Volatile, Semi-Volatile and Pesticide Laboratories) for specific details on safety and hazardous waste management.

12. DETERMINATION OF METHOD DETECTION LIMITS:

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12.1 **Determination of Method Detection Limits and Demonstration of Capability**

Refer to the SOP **LB-007** *Procedure and Policy for Method and Instrument Validation* and refer to SOP **LB-031** *Limit of Detection Verification* for specific procedural details

The LOD and Demonstration of Capability (DOCs) shall be determined for each main quality system matrix group identified by NELAP (air, drinking water, non-potable water, biological materials and solids/chemical materials). These groups represent the minimum matrix distinctions for LOD determinations and DOCs where there is evidence that the method performance will not be affected by sub-

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matrix distinctions within these group, Otherwise LODs and DOCs shall be determined separately for the quality system matrix sub-groups listed below. Where a suitable matrix cannot be found for preparing samples for LOD determinations or DOCs, another similar matrix type may need to be used or samples may need to be prepared in the absence of a matrix (e.g. method blanks). Reasons for matrix substitution may include (but are not limited to): inappropriate background analyte levels in the matrix for the intended study, no analyte-free matrix is available for method blanks, no reference materials are available for a matrix, etc,

12.1.1 Quality System Matrices:

- Aqueous – all aqueous samples excluding drinking water (see below) and salt or estuarine waters;
- Drinking Water – water from a designated potable source;
- Saline/Estuarine – an aqueous sample from an ocean or estuarine. The effects of this matrix type may vary from analysis to analysis and with salt content. Therefore, the decision to what extent if any this matrix has on the LOD and what salt levels may affect the LOD is left to the discretion of experienced supervisory staff;

12.1.2 MDL Determination Procedures

12.1.2.1 The MDLs were established using procedures given in EPA Chapter 40 Part 136, Appendix B of the Federal Register. Also refer to **Reference 13.1 and 13.2.**

12.1.2.2 Seven replicate samples are analyzed near the MDL. The MDL is the concentration of analyte at which there is analyte present with 99% confidence.

12.1.2.3 The results of the seven replicate data sets are tabulated and the statistical calculations are performed electronically on at least an annual basis to establish or update the MDLs and PQLs for each analyte and matrix. A list of MDLs is given in the Laboratory Comprehensive Quality Control Plan, see Reference 13.12.

TABLE 1: Components in Petroleum Hydrocarbon Standard (FL-PRO)

Octane (C_8)	Hexacosane (C_{26})
Decane (C_{10})	Octacosane (C_{28})
Dodecane (C_{12})	Triacontane (C_{30})
Tetradecane (C_{14})	Dotriacontane (C_{32})
Hexadecane (C16)	Tetratriacontane (C_{34})
Octadecane (C_{18})	Hexatriacontane (C_{36})
Eicosane (C_{20})	Octatriacontane (C_{38})
Docosane (C_{22})	Tetracontane (C_{40})
Tetracosane (C_{24})	
Surrogates	
Nonatriacontane (C_{39})	ortho-Terphenyl (OTP)
Pattern Identification Standards	
Unleaded Gasoline	Kerosene

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Diesel Fuel #2	Motor Oil
25% Weathered Diesel Fuel #2	Jet Fuels
50% Weathered Diesel Fuel #2	Fuel Oils
75% Weathered Diesel Fuel #2	Transmission Fluids

TABLE 2: Components in Hydrocarbon Standard (EPH): Compound specific information is listed in parenthesis after each compound. Each n-alkane's mass spectrum is nearly identical with each of the others. Also, the molecular ion (M/Z=1) is essentially unobservable for all but the lightest Aliphatics. This makes spectral speciation of normal alkanes by MS difficult. Fortunately chromatographic identification is practical since their retention times follow a classic, almost rhythmic retention pattern and the separation is excellent. Conversely, the aromatics have very specific and readily observable molecular ions as well as characteristic secondary ions making it possible to precisely identify them despite shifts in retention times and co eluting compounds. Components in the Aliphatic Hydrocarbon Standards:

n-Nonane (C_9)	n-Eicosane (C_{20})
n-Decane (C_{10})	n-Docosane (C_{22})
n-Dodecane (C_{12})	n-Tetracosane (C_{24})
n-Tetradecane (C_{14})	n-Hexacosane (C_{26})
n-Hexadecane (C_{16})	n-Octacosane (C_{28})
n-Octadecane (C_{18})	n-Triacontane (C_{30})
n-Nonadecane (C_{19})	n-Hexatriacontane (C_{36})
Surrogate	
1-Chloro-octadecane	

TABLE 3: Components in the Aromatic Hydrocarbon Standards:

Naphthalene	Benzo(a)anthracene
2-Methylnaphthalene	Chrysene
Acenaphthalene	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	
Surrogate: ortho-Terphenyl	
2-Bromonaphthalene (Fractionation Surrogate)	2-Fluorobiphenyl (Fractionation Surrogate)

TABLE 4: MDLs and PQLs for FL-PRO & EPH Methods:

	Water mg/L	Sediment mg/kg

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Analyte	MDL	PQL	MDL	PQL
TRPH	0.25	1	19	77
$C_{11} – C_{22}$ Aromatics	0.05	0.2	5	20
$C_9 – C_{18}$ Aliphatics	0.02	0.08	2	8
$C_{19} – C_{36}$ Aliphatics	0.03	0.12	3	12

13. REFERENCES

13.1 Method for Determination of Petroleum Range Organics. Florida Department of Environmental Protection.

13.2 Method for Determination of Extractable Petroleum Hydrocarbons (EPH). Massachusetts Department of Environmental Protection.

13.3 DEP SOP SV-004. Extraction and Fractionation of Petroleum Range Organics from Waters and Sediments (FL-PRO and MADEP-EPH)

13.4 DEP SOP SV-006. Analysis of Base/Neutral/Acid Extractables by Gas Chromatography/Mass Spectrometry

13.5 DEP SOP SV-009. BNA Standard Preparation.

13.6 DEP SOP LB-027. Standard Operating Procedure for Reporting Qualified Data.

13.7 DEP SOP SV-011. BNA Group Data Review/Authorization Checklist.

13.8 DEP SOP SV-010. Quality Assurance/Quality Control in the Semi-Volatile Organics Laboratory (BNA-GC/MS).

13.9 DEP SOP OG-001. Safety and Waste Management Practices in the Organic Analysis Groups (Volatile, Semi-Volatile and Pesticide Laboratories).

13.10 Florida Department of Environmental Protection, Standard Operating Procedure **LB-007** *Procedure and Policy for Method and Instrument Validation.*

13.11 Florida Department of Environmental Protection, Standard Operating Procedure **LB-031** *Limit of Detection Verification.*

13.12 Comprehensive Quality Assurance Plan, Chemistry Section, Bureau of Labs, DEP, 2010.

Appendix of Changes

08/06/2010 Elaborated MDL determination in section 12.1 to include different matrices and supporting references in section 13.

11/17/2010 Added sections 1.3 to 1.5 and 6.11 to include details on pattern recognition.

11/29/2011 Specified calibration standards concentration. Elaborated on calibration fit requirements. Added surrogate recovery limits table. Other editorial changes.

10/09/2014 Network directory changes for backup and upload files.

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10/07/2015 Network directory changes for backup and upload files, added matrix spikes control limits in 7.5.3. The difference between ICV and CCV clarified in section 6.6.

09/21/2017 Enviroquant software replaced with Masshunter. MDLs updated.

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