STANDARD OPERATING PROCEDURE

For

FL-PRO

DETERMINATION OF PETROLEUM RANGE ORGANICS

SOP Revision Log for AEL SOP SVOC-004

Revision Numb	Revision Dat	Reason for Revision	Section(s) and Page(s) Revise
Revision 00	1/30/01	Initial Creation in this format	All sections affected
Revision 01	11/11/04	Re-edit of SOP	All sections affected
Revision 02	1/14/05	Re-edit of SOP	All sections affected
Revision 03	2/08/07	Redefine Detection level section 3, Expand section 4 and 6, rewrites of sections 8, 10, 11 12, 14, 20, update references section 22, add analyst to iDOC list section 23	Sections 3, 4, 6, 8, 10, 11, 12 14, 20, 22, 23
Revision 04	3/31/09	Update curve points in section 10, add analyst in section 23, iDOC performance	Sections 10 and 23
Revision 05	5/15/10	Re-write of section 1, expanded sections 6, 1 Edits to sections 7,14,16, added section 22 maintenance, renumbered sections 22,23	Sections 1, 6, 7, 13,14, 16, 22 23, 24
Revision 06	8/26/11	Add tables for speciation and fingerprinting Sections 15, 24. Add language on how to integrate and calculate surrogate recoveries. Edits to language throughout.	All sections affected
Revision 06	10/31/12	Add example for calculating spike volumes on final concentrations and LIMS entry.	Section 15
Revision 07	3/28/2014	Allow the use of a 250ml extraction and analysis. Analysts referenced for validating method updated to most current IDOC holder.	Sections 1, 9, 14, 15, 24
Revision 07	6/6//2014	To section 1.2-clarified by adding extraction on "soils" to use sonication. To Section 14.2.1 added "The volume of extraction solvent will still be same amounts as listed in 14.6 through 14.9. (60mls per shake)."	Sections 1.2, 14.2.1
Revision 07	10/28/14	Section 1.1 added in that 1ml volumes for spik and final volumes are in use. Section 14.2 thr 14.10, reworded procedure to mark bottles an wait until after extraction to measure volume. Sample taken directly from bottle, with bottle being rinsed with solvent. Section 9.17 colum in use is 30 meters.	Sections 1, 9, 14

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1.0 Identification of Test Method

1.1 Method FL-PRO, Method for determination of Petroleum Range Organics

1.2 This SOP deviates from the Method for Determination of Petroleum Range Organics (Method #FL-PRO) Revision 1, Nov 1, 1995 Florida Department of Environmental Protection in the following areas: Standards are all purchased from certified vendors and are not made from stock reference materials. Add only 1.0 mL each of the surrogate spiking solution with OTP at 50ppm and C39 at 300 ppm into each sample instead of 2.0 mL each. Initial Calibration is performed using 7 concentration levels at 25, 50, 100, 200, 300, 400 and 500 μg/mL of each individual component versus the suggested 6 concentration levels at 5, 50, 150, 250, 350 and 500 μg/m. This is equivalent to 425, 850, 1700, 3400, 5100, 6800, and 8500 μg/mL total alkanes in the standards. Extractions on soils are done ultrasonically in sonication baths. A 1 ml spiking volume is being used instead of the 2ml volume listed in the method. A final concentration volume of 1ml is being used instead of the 2ml volume listed in the method. These deviations from the referenced test method represent equivalent or improved performance over the referenced test method conditions.

1.3 This SOP also deviates from the from the Method for Determination of Petroleum Range Organics (Method #FL-PRO) Revision 1, Nov 1,1995 Florida Department of Environmental Protection in that it allows for a smaller sample volume of **250mls** versus the method listed volume of **1000mls** when extracting aqueous samples. This deviation from the referenced test method has been proven to be equivalent in performance when compared to the referenced test method.

2.0 Applicable Matrix or matrices

2.1 This method is applicable to aqueous samples, including wastewaters, ground waters, surface waters, and leachates as well as soils or sludges.

3.0 Detection Limit

3.1 The method detection limit is determined in accordance with AEL SOP ADMIN-012, referencing 40CFR136, appendix B.

3.2 For the current MDLs, see the electronic version specific for the method, instrument, and matrix on the designated Quality Assurance (Q) drive of the AEL networked servers.

4.0 Scope and Application, including components to be analyzed

4.1 Analytes

4.1.1 This method is designed to measure the concentration of Petroleum Hydrocarbons in water and soil in the alkane range of C_8 - C_{40}.

4.1.2 The intent is to provide an accurate estimate of petroleum concentration in environmental samples in the above stated C-Range (nominally diesel through motor oils).

4.2 Dynamic Range

4.2.1 Dilutions should be performed as necessary to put the chromatographic envelope within the linear range of the method. Linear range is dependent in part upon column type, detector sensitivity and injection volume. Typically, the approximate range is 170 - 17,000 ng on column of Total PHS. Each laboratory must establish and document the linear range for the instrument(s) in use in the laboratory.

4.3 Experience

4.3.1 This method is based on a solvent extraction, gas chromatography (GC) procedure. This method should be used by, or under supervision of, analysts experienced in the use of solvent extractions and gas chromatographs. The analysts should be skilled in the interpretation of gas chromatograms and their use as a quantitative tool.

4.4 Fingerprinting

4.4.1 An experienced analyst may be able to recognize similar patterns between sample chromatograms and purchased reference materials. With these reference chromatograms to overlay (such as purchased kerosene or a pure product delivered by the client), a case narrative may include language that tentatively identifies a "fingerprint pattern" while also stating the range of the chromatographic pattern. (Diesel range, gasoline range, etc.) However, care should be taken not to draw a definitive match, as this method is limited to a qualitative determination only. Weathering can greatly affect the patterns as compared to new product. See appendices at the end of this SOP for some illustrations of fingerprint patterns.

5.0 Summary of Method

5.1 One liter of water or twenty-five grams of soil is spiked with two surrogates and extracted with methylene chloride. The extract is removed from the soil or water, filtered through a drying column consisting of anhydrous sodium sulfate on the top layer to remove water and silica gel on the bottom layer to remove potential organic interferences. The extract is concentrated to a volume of 1.0 mL. An aliquot is injected onto a capillary column gas chromatograph (GC) equipped with a flame ionization detector (FID). Quantitation is based on the detector response compared to a series of normal alkane standards.

5.2 This method is based in part on USEPA Methods 8000 and 8100, SW-846, "Test Methods for Evaluating Solid Waste", 3rd Edition (1), Method OA-2 (3), work by the EPA UST Work Group "Measurement of Petroleum Hydrocarbons: Report on Activities to Develop a Manual", 1990 (11), Method AK103.0, Revision 2 (12), PUBL-SW-141, July 1993 (13) and the Florida Department of Environmental Protection Technical Advisory Committee for 62-770, F.A.C, Petroleum Contamination Site Cleanup Criteria.

5.3 If a non-aqueous liquid or waste solid is to be extracted, weigh 1gram of sample and dilute to 10mls with MeCl. Spike with surrogates. Pass the sample through a column of sodium sulfate to dry then proceed to a silica gel cleanup as outlined in Section 14.

5.4 Fingerprint or pattern recognition can be performed under this method as described in Section 14.

6.0 Definitions

See also AEL ADMIN SOP-039 Laboratory Definitions

6.1 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.

6.2 Petroleum Hydrocarbon Standard: A 17-component mix of all even - numbered normal alkanes from C_8 to C_{40} (Appendix 1). This standard serves as a quantitation standard and a retention time window defining Petroleum Hydrocarbons. CCV: Continuing Calibration Verification - injected at the beginning of a 12- hour analytical shift and end of an analytical batch to confirm calibration throughout the run. CCVs also must also be run every 10 samples and at the close of a sequence. QC spikes and method blanks are not considered as sample runs when setting the sequence. A typical sequence for a batch of 20 samples could be IB, CCV, MB, LCS, MS, MSD, samples 1-10, CCV, IB, samples 11-20, closing CCV.

6.2 ICV: Initial Calibration Verification – injected after the initial calibration of an instrument in order to verify the initial calibration. If the response (or calculate concentration) for any analyte is within +/- 20 % of the initial calibration response per analyte then the ICV is considered valid.

6.3 Laboratory Control Sample, (LCS), also referred to as Laboratory fortified blank (LFB):a quantity of reagent water to which known quantities of analytes are added in the laboratory. The LCS is analyzed exactly like a sample with its purpose being to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements.

6.4 Laboratory Control Sample Duplicate: (LCSD) a second quantity of reagent water to which known quantities of analytes are added in the laboratory. The LCSD is analyzed exactly like the LCS with its purpose being to determine whether the laboratory is capable of obtaining accurate and reproducible measurements.

6.5 Method Blank, (MB), also referred to as Laboratory reagent blank (LRB): a quantity of reagent water that is treated exactly as a sample including exposure to all equipment, acids, and internal standards. Standards that are used with other sample. The MB is used to determine if method analytes or other interferences are present in the laboratory environment, reagents or other materials.

6.6 Matrix Spike, (MS), also referred to as Laboratory fortified matrix,(LFM): An aliquot of a client supplied sample, that is chosen at random, to which known quantities of the method analytes are added in the laboratory. The MS is analyzed exactly like the sample with its purpose being to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the values in the MS corrected for the background concentration. Matrix Spikes are analyzed with every batch or per 20 samples.

6.7 Matrix Spike Duplicate: (MSD) A second aliquot of a client supplied sample to which known quantities of the method analytes are added in the laboratory. The MSD is analyzed exactly like the MS with is purpose being to confirm Matrix bias and determine whether the laboratory is capable of obtaining reproducible and accurate results. Matrix Spike Duplicates are analyzed with every batch or per 20 samples

6.8 Case Narrative (CN) -- A case narrative is simply a means of describing exactly what transpired with the samples during the analytical process. Case narratives are required for variances that occur within a project.

6.9 Non-Conformity Form (NCF) -- Form which will be completed and processed for each QC failure or deviation from normal protocol that occurs outside the scope of normal operation as defined by the AEL QM Section 10, AEL SOP Admin-016 and Method SOP.

6.10 Standard -- A solution prepared by diluting stock standard solutions used to calibrate the instrument response with respect to analyte concentrations. Also referred to as calibration standards (CALS) as in section 10.10.

6.11 Stock Standard -- A concentrated solution containing method analytes that is purchased from a commercial source having Certificates of Analysis.

6.12 Surrogate Analyte (SA) -- A pure analyte(s), which is extremely unlikely to be found in any sample, and which is added to a sample aliquot in known amount(s) before extraction and is measured with the same procedures used to measure other sample components. The purpose of a surrogate analyte is to monitor method performance with each sample.

6.13 Stock Standard Solution (SSS) -- A concentrated solution containing a single certified standard that is a method analyte, or a concentrated solution of a single analyte prepared in the laboratory with an assayed reference compound. Stock standard solutions are used to prepare primary dilution standards.

6.14 Primary Dilution Standard Solution (PDS) -- A solution of several analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration solutions and other needed analyte solutions.

6.15 Calibration Standard (CAL) -- A solution prepared from the primary dilution standard solution and stock standard solutions of the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

6.16 Quality Control Sample (QCS) -- A sample matrix containing method analytes or a solution of method analytes in a water miscible solvent which is used to fortify reagent water or environmental samples. The QCS is obtained from a source external to the laboratory, and is used to check laboratory performance with externally prepared test materials.

6.17 Material Safety Data Sheets (MSDS): Written information provided by vendors concerning a chemical's toxicity, health hazards, physical properties, fire and reactivity data, including storage, spill and handling precautions.

6.18 Analytical Batch: The set of samples started through the analytical process to a maximum of 20 field samples. A Method Blank, a Laboratory Control Sample, and a Sample Duplicate of at least one of the field samples, if available, must accompany each analytical batch of 20 or fewer samples.

6.19 LOD - Limit of Detection (LOD): LOD is **not** synonymous with MDL. LOD is an estimate of the minimum amount of a substance that an analytical process can reliably detect with a high level of confidence (99% Confidence, that is a false negative rate of 1%) An LOD is analyte, prep method, cleanup method, analysis method, and matrix specific and is laboratory dependent. The LOD is at the level of the MDL verifications. The LOD when used as the MDL verification must go through all the same processes that a sample will go through and be detected above instrument noise level.

6.20 Limits of Quantitation (LOQ): The minimum levels, concentrations, or quantities of a target variable (e.g. target analyte) that can be reported with a specific degree of confidence. It is also the lowest concentration that produces a quantitative result within specified limits of precision and bias. For DOD work the LOQ will be set at or above the concentration of the lowest initial calibration standard. For DOD work the LOQ will be the concentration at which the PQL is verified. The LOQ can equal the PQL, but is not synonymous with the PQL.

6.21 Limits of Quantitation (LOQ) Verification: LOQ verifications are a spiked clean matrix sample that must go through all the same processes that regular samples will go through and be within the precision and bias acceptance criteria of the method. The LOQ verifications are spiked at the concentrations of the LOQ.

6.22 Method Detection Limit: (MDL) – an estimate of the minimum amount of a substance that an analytical process can readily detect. The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero. Is determined most often as 3.14 times the standard deviation of a low level seven replicate study, however can be determined for some methods as the lowest increment measurable with confidence. MDLs are determined for each analyte, matrix, prep method, cleanup method, analysis method, and instrument. (See each method's requirements). The MDL is one way to establish a Detection Limit, not a Limit of Detection.

6.23 Method Detection Limit: **(**MDL) Verification**:** MDL verifications are a spiked clean matrix sample that must go through all the same processes that a regular sample will go through and be detected above instrument noise level. For labs accredited under DOD ELAP, the MDL verifications must be performed immediately after the initial MDL study and on a quarterly basis thereafter. For labs accredited under NELAC (TNI) Standards only, MDL verifications are to be performed immediately after the initial MDL study and on a yearly basis thereafter.

6.24 Practical Quantitation Level (PQL): the lowest calibration standard or lowest quantitation level for the method and matrix. The concentration below which data is to be qualified as having less certainty. PQLs are at a **concentration greater than that of the MDL.**

6.25 Qualifier Codes (For Florida and FDEP work)

6.25.1 A - Value reported is the mean (average) of two or more determinations. This code shall be used if the results of two or more discrete and separate samples are averaged. These samples shall have been processed and analyzed (e.g. laboratory replicate

samples, field duplicates, etc.) independently. Do not use this code of the data are the result of replicate analyses on the same sample aliquot, extract or digestate. Under most conditions, replicate values shall be reported as individual analyses.

6.25.2 I - The reported Value is between the laboratory method detection limit (MDL) and the laboratory practical quantitation limit (PQL).

6.25.3 K- Off scale low.

6.25.4 L- Off scale high. Use if reporting above the acceptable level of quantitation.

6.25.5 U- Indicates that a compound was analyzed for but not detected. The value associated with the qualifier will be the MDL.

6.25.6 V- Indicates that the analyte was detected in both the sample and the associated method blank. NOTE: The method blank value **cannot** be subtracted from the associated sample to give a result. The sample result will be reported as is with the "V" qualifier.

6.25.7 H - Value based on field kit determination; results may not be accurate. This code shall be used if a field-screening test (i.e. field gas chromatograph data, immunoassay, vendor-supplied field kit, etc.) was used to generate the value and the field kit or method has not been recognized by the Department as equivalent to laboratory methods.

6.25.8 O - Sampled, but analysis lost or not performed. Note: if reporting data to STORET, a numerical value must be entered. Such values are not meaningful and shall not be used.

6.25.9 Q - Sample held beyond the accepted holding time. This code shall be used if the value is derived from a sample that was prepared and/or analyzed AFTER the approved holding time restrictions for sample preparation and analysis.

6.25.10 Y - The laboratory analysis was from an unpreserved or improperly preserved sample. The data may not be accurate.

6.25.11 REJ - Data is rejected and should not be used. Some or all of the quality control data for the analyte were outside criteria, and the presence or absence of the analyte cannot be determined from the data.

6.25.12 NAI - Not analyzed due to interference

6.25.13 J - Estimated value; value not accurate. This code shall be used in the following instances:

6.25.13.1 "1" Surrogate recovery limits have been exceeded;

6.25.13.2 "2" No known quality control criteria exists for the component;

6.25.13.3 "3" The reported value failed to meet the established quality control criteria for either precision or accuracy;

6.25.13.4 "4" The sample matrix interfered with the ability to make any accurate determination; or

6.25.13.5 "5" The data is questionable because of improper laboratory or field protocols (e.g. composite sample was collected instead of a grab sample).

6.25.13.5.1 A "J" value shall be accompanied by justification for its use.

6.25.13.5.2 A "J" value shall not be used if another code applies (ex. K, L, M, T, V, Y, PQL)

6.25.13.5.3 If more than one code applies, and the data is to be entered into STORET, only one code shall be reported. The code shall be selected based on the following hierarchy: REJ, NAI, O, Y, V, H, J, B, K, L, M, PQL, T, Z, A

6.26 Abbreviations used in sample preparation logbooks, data printouts and other areas- Organics abbreviations for this method:

RR Rerun/Reanalyze
CF Confirmation
DIL Dilution
STD Standard
STR Straight/No Dilution
SURR Surrogate
INT Internal Standard
WRT Wrong Retention Time
IS/SURR Internal Standard/Surrogate
INT STD Intermediate Standard
MeCl2 Methylene Chloride
CS2 Carbon Disulfide

7.0 Interferences

7.1 Other organic compounds, including chlorinated hydrocarbons, phenols, and phthalate esters are measurable. As defined in the method, the Petroleum Range Organics method results include these compounds.

7.2 Animal and vegetable oil and grease and biogenic terpenes are also measurable if the sample is not cleaned up before analysis. In order to eliminate false positives from these sources, **the silica cleanup is a mandatory part of this procedure**.

7.3 High purity reagents (pesticide grade or better) must be used to minimize interference problems.

7.4 Washing all glassware per SOP ADMIN-034 reduces Method interferences. At least one reagent blank must be analyzed with each batch or for every 20 samples to demonstrate that the samples are free from method interferences.

7.5 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. Three between sample rinsings are automatically performed by the Perkin Elmer autosystems, which is configured during initial instrument configuration. Whenever an unusually concentrated sample (any sample at the highest point of the curve or greater) is encountered, it will be followed by an analysis of a solvent blank to check for instrument contamination. If a "hot" sample is not discovered until after an analytical batch has been completed, any samples that were not below detection levels and run after the "hot" sample will be rerun under new instrument QC (passing CCVs and instrument blank) to confirm that any hits are confirmed and at accurate amounts.

8.0 Safety

8.1 Refer to the AEL Chemical Hygiene Plan and Safety Manual for safety precautions and for the Hygiene Plan and Emergency Response Plan.

8.2 See Standard Methods, 21st Edition, Section 1090 Laboratory Occupational Health and Safety.

9.0 Equipment and Supplies

9.1 Glassware - All specifications are suggested only: 4 oz. amber glass wide mouth jars with Teflon®-lined screw caps (solid samples) and 1 liter amber glass containers with Teflon®-lined screw caps (aqueous sample).

9.2 Separatory funnel - 2-liter, with polytetrafluoroethylene (PTFE) stopcock. For smaller aqueous volumes, smaller separatory funnels can be used.

9.3 Automatic Separatory funnel Auto-shaker

9.4 Disposable borosilicate pipets

9.5 80mm glass powder-funnel

9.6 Large Volume (200-500mL) concentration system Turbo-Vap consisting of a temperature controlled warm water bath. Each unit concentrates six samples simultaneously with a flow of nitrogen gas. See section 7 of the Quality Manual for further information on the Turbo-Vap concentrator.

9.7 Vials - 2-mL, glass with PTFE-lined screw caps.

9.8 pH indicator paper - pH range including the desired extraction pH.

9.9 Gas-tight micro-syringes: 10.0ul, 25ul, 50ul, 100ul, and 1ml.

9.10 Graduated cylinder – 1.0 Liter.

9.11 Apparatus for grinding dry waste samples.

9.12 Sonicator, Branson Model 8510 or equivalent.

9.13 Beakers - 400-mL.

9.14 Balance - Top-loading, capable of accurately weighing to the nearest 0.01 g.

9.15 Spatula - Stainless steel or PTFE.

9.16 Gas Chromatograph: A Perkin Elmer Autosystems Gas Chromatograph with Flame Ionization Detector (FID). For data collection and processing, the Perkin Elmer brand “Turbochrom” software is used. Reference section 7 of the Quality Manual for further information on the instrumentation.

9.17 Column: 30 meter X 0.25 mm ID J&W DB-5 or equivalent with 0.25 micron film thickness.

9.18 #4 Whatman filter paper-125mm diameter.

10.0 Reagents and Standards

10.1 Reagents are ordered and tracked in accordance with SOP's ADMIN-013 and ADMIN-031.

10.2 The mixing of reagents shall be tracked in a reagent logbook kept in the extractions room and will contain the following information: for parent materials the lot number, manufacturer name, chemical name, expiration date, AEL receiving lot#, amount used, how it was mixed, and then the newly created reagent will have a lot #, the date it expires, and its concentration. Examples of this would be the cutting of acid 1:1 and the mixing of sodium hydroxide.

10.3 Reagent grade (or better) chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the 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 sufficiently high purity to permit its use without lessening the accuracy of the determination. Reagents should be stored in glass to prevent the leaching of contaminants from plastic containers.

10.4 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, which will be from the di water tap. Seimens Company in accordance with Admin-032 maintains our present di water system.

10.5 Methylene chloride, hexane, acetone, carbon disulfide - pesticide grade or better in accordance with ADMIN-013.

10.6 Sodium sulfate - (ASC) granular, anhydrous. Purify by heating at 400°C for 4 hours in a shallow tray.

10.7 Stock standard solution - Prepare the following stock standards. Unless noted, all are prepared in the methylene chloride listed in section 10.2.

10.7.1 Surrogate Standards: 10,000 µg/mL ortho-terphenyl (OTP) and 3000 µg/mL nonatriacontane (C_{39}). A working solution is made at 50 µg/mL (OTP) and 300 µg/mL (C_{39}) in acetone and carbon disulfide respectively (a water soluble solvent). One ml to be added to all samples, quality control, standards, and blanks samples before extraction.

10.7.2 Individual stock solutions of C_8 - C_{40} even normal alkanes (see Appendix 1). For solubility reasons, it is necessary to prepare stock solutions of n-alkanes in solvents of acetone and carbon disulfide.

10.7.3 Petroleum Hydrocarbon Standard: C_8 - C_{40} even normal alkane standards with each component at 2000 µg/mL. Calibration levels are mixed from this stock standard solution at levels of 25, 50, 100, 200, 300, 400, and 500 µg/mL of each individual component. This is equivalent to 425, 850, 1700, 3400, 5100, 6800, and 8500 µg/mL total alkanes in the standards and **is defined as TOTAL PHS**. See section 13.1 for instruction on how to mix standards.

10.7.4 Silica gel

10.7.4.1 Silica gel, 60 to 200 mesh, Davidson Grade 950 or equivalent (deactivated with 1 to 2 percent water).

11.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

11.1 See AEL Quality Manual section 6.0 for sample acceptance policy.

11.2 See AEL Admin-005 and Admin-023

11.3 See FDEP SOP FS1000 for preservation requirements, shipping conditions, and holding time requirements.

12.0 Quality Control

12.1 The laboratory must establish the ability to generate data of acceptable accuracy and precision. Minimum quality control requirements are an initial demonstration of capability (iDOC) study, laboratory control spikes, matrix sample spikes and spike duplicates, instrument blanks, extracted (method) blanks, and continuing calibration checks. Additional QC practices may be added. (Reference Quality Manual section 3.0 for iDOC record keeping procedures.)

12.2 The Demonstration of Capability shall consist at a minimum of a method blank and 4 replicates spiked with a standard different than that used to make the curve. (Separate source standard).

12.3 The initial demonstration of capability study for water needs 55-118% recovery and an RSD of 20% or less to pass. The initial demonstration of capability study for soil needs 63-153% recovery and an RSD of 25% or less to pass.

12.4 The Demonstration of Capability is not considered complete until the analyst has signed a statement saying that they have read, understood, and agreed to follow the AEL-SOP for this method and the associated EPA and/or Standard Methods on which the AEL-SOP was based.

12.5 Initial DOC's must be successfully performed by each analyst in accordance with the Quality Manual and ADMIN-030.

12.6 The laboratory must, on an ongoing basis, demonstrate through the analysis and evaluation of quality control check standards and continuing calibration standards that the operation of the measurement system is in control.

12.7 After successful calibration, analyze the reagent blank sample, which must be prepared with every analytical batch or sequence. The surrogate recovery must be within established limits and the calculated TRPH value of the blank shall be at or below the established method detection limit.

12.8 For every batch of 20 samples or less, a matrix spike sample and matrix spike duplicate sample or laboratory control sample duplicate shall be processed, analyzed and evaluated. The accuracy of the spiked samples and the precision of the duplicate samples must be within established limits. (see section 16.0)

12.9 A Calibration check standard must be analyzed every 10 billable samples. QC spikes and method blanks are not considered as sample runs when setting the sequence. A typical sequence for a batch of 20 samples could be IB, CCV, MB, LCS, MS, MSD, samples 1-10, CCV, IB, samples 11-20, closing CCV.

12.10 If any of the above criteria are not met, the problem must be corrected before samples are analyzed.

12.10.1 If the matrix spike(s) are not within method specified limits, the results of the laboratory control samples or quality control check samples should be assessed. If the results of the latter two quality control checks are acceptable, the problem with the matrix spike(s) may be attributed to matrix interferences, and the analysis of the sample set may proceed. See 18.0 and 19.0 of this method for how data that has not met all passing criteria is to be handled.

12.11 The surrogate standard recoveries in each sample must be calculated. **Unlike the calculation of petroleum hydrocarbons, the response must be based on a valley-valley integration of the peak response.** If recoveries are outside method limits, verify calculations, dilutions, standard solutions and instrument performance.

12.11.1 High recoveries may be due to a co-eluting matrix interference or the presence of high molecular weight contaminants; examine the sample chromatograph.

12.11.2 High recoveries may also be due to memory effects caused by poor sample volatility, backflash or carryover. Check instrument conditions, injection volume and injector temperature.

12.11.3 Low recoveries may be due to adsorption by the same matrix.

12.11.4 Low recoveries may also be caused by incorrect integration. The chromatographic profile of motor oils does not give baseline resolution of all components, resulting in a characteristic rise in baseline underneath the resolved hydrocarbon components known as the "unresolved complex mixture", or UCM. Do not use peak-to-peak integration, use forced baseline integration.

12.11.5 If the surrogate recovery is outside of established limits, the results must be flagged and an explanation offered in a case narrative.

12.11.6 Equipment blanks and field collected duplicates (if required) shall be analyzed with the associated sample set.

12.11.7 See attached acceptance/rejection policy for data generators in the organics department in Appendix 3 (Sect. 23.3).

13.0 Calibration and Standardization

13.1 Initial Calibration - Calibration shall be by external calibration using a minimum of 5 concentration levels for the initial calibration. Quantitation shall be by calibration factor or linear regression. A calibration factor should be attempted first. See AEL ADMIN-SOP-038, section 3.3 for selection of curve fit and curve type. In general, a calibration factor with an rsd of 20% or less is most often used to calculate sample recoveries. Linear regression is only used if the rsd criteria cannot be met.

13.1.1 Calibration

Primary Standards

A. Florida TPH Mix Primary Standard is at 2000 ug/mL.
B. Florida TPH Mix Secondary Standard is at 2000 ug/mL.
C. Orthoterphynl (OTP) Surrogate Standard is at 10000 ug/mL.
D. Nonatricontane (C39) Surrogate Neat Standard is pure > 97.0% (GC).

Intermediate standards for Surrogates

E. 1000 mg/L OTP = 100uL of 10,000 mg/L OTP **(C.)** + 900uL Methylene Chloride (MECL)
F. 3000 ppm C39 Intermediate Standard = 0.7500 g. of C39 Neat Std **(D.)** + 250 mL of Carbon Disulfide (CS2)

FL-PRO CURVE: To mix, syringe amounts listed for A, E, and F into MECL for final volume of 1ml at concentrations in mg/L as listed in **Bold**.

Primary TRPH Final Concentratio	AMT **A** **(uL)**	OTP Final conc	AMT **E** **(uL)**	C39 Final conc.	AMT **F** **(uL)**	MECL (uL)
25	12.5	**20**	20	**90**	30	937.5
50	25	**30**	30	**180**	60	885
100	50	**40**	40	**270**	90	820
200	100	**50**	50	**360**	120	730
300	150	**60**	60	**450**	150	640
400	200	**70**	70	**540**	180	550
500	250	**80**	80	**630**	210	460

ICV 100 = 50uL Secondary TRPH (2000 mg/L) + 100uL C39(3000 mg/L) + 5uL OTP(10,000 mg/L) + 845uL MECLL2

13.2 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 C_8 to a point past C_{40} when a heavy motor oil would be expected to return to baseline. All responses must be determined as responses to baseline and not valley to valley. The selection of the time interval (i.e. time from beginning to end of integration) should be based on injection of appropriate pattern recognition standards and **must be constant for all standards and samples**.

13.3 If the percent relative standard deviation of the calibration factor is less than or equal to 20% over the working range, the linearity through the origin can be assumed and the average calibration factor can be used in place of a calibration curve.

13.4 Linear Regression - If a calibration factor cannot be used then a linear regression shall be calculated using the area of the total PHS area versus the PHS concentration. The correlation coefficient shall be equal to or greater than 0.995.

13.5 The accuracy of the initial calibration shall be verified by injecting a midpoint concentration of a standard mix that has been obtained from a different source (i.e., different vendor). **The calculated value shall be within ±20% of the expected value for this ICV.**

13.6 If the initial calibration fails any of the above criteria, a new set of standards shall be prepared, analyzed and evaluated prior to analyzing any samples.

13.7 Continuing Calibration - The working calibration factor or calibration curve must be verified on each working day, every 10 samples, and at the end of an analytical batch by the injection of a continuing calibration verification standard (CCV) at varied low and midpoint concentrations such as 50ppm and 100ppm standards. The initial standard must be evaluated prior to the analysis of any samples. For samples to be reportable, they must be bracketed by two passing **CCVs**. If the response for these standard varies from the predicted response by more **than ±25%,** the standards have failed and the instrument must be checked by the reanalysis of a new CCV. If the CCV passes, re-shoot it again to prove that it was correct. If it passes a second time, analysis may continue. If it fails on the first or second re-shoot, a new initial calibration curve must be prepared and verified before samples are analyzed.

13.8 Retention Time Window - The retention time window for the surrogates and C_8 and C_{40} shall be within the established range as determined in the retention time window study. This study is on file in the Semivolatiles room. If they are out of acceptance range, check for leaks, low pressure on the column gas, or perform maintenance as required. If it is determined that the times have shifted due to normal operation such as an adjustment to column flow or the shortening of the column, generate a new retention time study. (See AEL SOP-TECH-010 for procedures on "Establishing and Maintaining Retention Time Windows".)

13.9 Retention Time Window Study (See AEL SOP-TECH-010 for procedures on "Establishing and Maintaining Retention Time Windows".)

13.9.1 Before establishing windows, be certain that the GC system is within optimum operating conditions. Make three injections of the method standard throughout the course of a 72-hour period. Serial injections over less than a 72-hour period result in retention time windows that are too tight.

13.9.2 Calculate the standard deviation of the absolute retention times for the two surrogates, C_8, and C_{40}.

13.9.2.1 The retention time window for individual peaks is defined as a plus or minus three times the standard deviation of the absolute retention time for each component.

13.9.2.2 In those cases where the standard deviation for a particular analyte is zero or below +/-0.05, the laboratory should use ±0.05 min as a retention time window.

13.9.3 The laboratory must calculate retention time windows for these standards on each GC column and whenever a new GC column is installed. The laboratory must retain the data.

14.0 Procedure

14.1 **Sample preparation—Water Matrix**—Seperatory Funnel Extraction

14.2 As the entire contents of the sample bottle are to be extracted, mark the level of sample on the outside of the bottle for later measurement. If high analyte concentrations are anticipated, a smaller sample volume may be taken and diluted to 1-L with organic-free reagent water, or samples may be collected in smaller sample bottles and the whole sample used. Any time a full volume is not used, note in the case narrative. For blanks and LCSs use DI water as outlined in section 10.4.

14.2.1 A smaller volume of 250mls can be used. Samples shall be collected in 250 mls bottles so that the full container can be used and rinsed with solvent. However, if being collected with extra volume for duplicate analysis and/or matrix spiking, a larger container can be used. The volume of extraction solvent will still be same amounts as listed in 14.6 through 14.9. (60mls per shake).

14.3 Transfer the sample from the sample bottle to the 2-liter separatory funnel.

14.4 Check and document the pH in the extraction logbook.

14.5 Using a gas-tight syringe, add 1.0 mL of the surrogate spiking solution with OTP at 50ppm and C39 at 300 ppm into each sample in the separatory funnel and mix well. At this time spike QC samples as well. At least one method blank, an LCS, a Matrix Spike and Spike Duplicate must be extracted with each batch defined as 20 samples or less.

14.5.1 If using a 250ml sample volume, spike as above, except at 1/4 of the spike amounts listed.

14.6 Use 60 mL of methylene chloride to rinse the bottle and transfer this rinse solvent to the separatory funnel.

14.7 Seal and shake the separatory funnel vigorously for 30 seconds with periodic venting to release excess pressure. Then place on the auto shaker for 2 minutes at a setting of 74.

NOTE: Methylene chloride creates excessive pressure very rapidly; therefore, initial venting should be done immediately after the separatory funnel has been sealed and shaken once. The separatory funnel should be vented into a hood to avoid exposure of the analyst to solvent vapors.

14.8 Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Pass the solvent extract through a glass powder-funnel filled with anhydrous sodium sulfate. The funnel should be resting on top of a Zymark Tube so that the extract can be collected.

14.9 Repeat the extraction two more times using fresh portions of solvent (Sects. 14.6 through 14.8) rinsing the bottle each time. Combine the three solvent extracts.

14.10 Once finished with extracting, fill each bottle used with tap water to the initially marked line. Then pour into a class A graduated cylinder to measure the volume used for extraction. Record that amount in the extraction logbook.

14.11 **Perform the concentration** using the Turbo-Vap Sample Concentrator

14.11.1 Before beginning Turbo-Vap concentration, turn on the Turbo-Vap unit and set the bath temperature to the desired temperature and document the actual temperature in the extraction log. Check the water level in all of the units. The water should be halfway up to the lower set of perforations in the back of the chamber. Make sure that the hood is on to collect all solvent vapor given off by the Turbo-Vap

14.11.2 There are four different options that can be programmed into the Turbo-Vap to stop the concentration process. The Turbo-Vap can be programmed to concentrate until it is manually shut off, to concentrate only for a certain period of time, to concentrate until a sensor indicates the endpoint is reached, or to concentrate for a certain period of time after the sensor endpoint is reached. Ensure that the Turbo-Vap is programmed to stop when a sensor endpoint is reached. If this option is selected, the Turbo-Vap should stop concentration when the sample volume is 1.0 mL. If any of the other options are selected, the sample may go dry.

NOTE: It is the practice here at this lab to not depend on the sensors to end the concentration. All samples are to be watched and manually completed. A dark sample can leave a residue on the tubes that will negate the sensors.

14.11.3 Place the Zymark tube containing the sample extract in the Turbo-Vap. The Turbo-Vap can concentrate up to six samples at one time. Press the start button the appropriate tube to be concentrated. This allows the Nitrogen gas to flow across the sample. Blow down the sample to about 10mls. Rinse the walls of the thimbles several times to bring back up to about 15mls. Repeat this at least once more as a residue will form on the thimbles that needs to be "pushed down" the sides.

14.11.4 The outside of the condenser may be covered in water droplets. Be sure that they do not drip into the sample extract.

NOTE: If the sample evaporates to dryness, re-extract the entire sample. The loss of analytes can be assumed.

14.11.5 Concentrate the sample extract to 1ml. If the sample extract will not concentrate to 1.0mL or less, is very viscous, or is very dark in color, make comments in the extraction log book, and this sample may need to be diluted up to a higher volume

CAUTION: When the volume of solvent is reduced much below 1 mL, semi volatile analytes may be lost. It is recommended not to go below 0.75 mLs and mandated that no samples are to go below 0.5mls during concentration in the turbovaps.

14.11.6 The extract may now be analyzed for the target analytes. Transfer to a 1 ml vial with a PTFE-lined screw cap or crimp top, and labeled appropriately.

Use a reference vial filled with one ml of reference solvent (filled using a 1ml syringe) to comparatively measure the 1ml of extract of each sample. All analyst should have a study to show that they can accurately measure out one ml of sample extract prior to doing this measurement technique, or they must use calibrated 1ml vials for transferring exactly 1ml to the vials.

14.12 Soil preparation - Sonication

14.12.1 Sediment/soil samples - Decant and discard any water layer on a sediment sample. Mix sample thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks

14.12.2 Dry waste samples amenable to grinding - Grind or otherwise subdivide the waste so that it either passes through a 1-mm sieve or can be extruded through a 1-mm hole. Introduce sufficient sample into the grinding apparatus to yield at least 10 g after grinding.

14.12.3 Gummy, fibrous, or oily materials not amenable to grinding should be cut, shredded, or otherwise reduced in size to allow mixing and maximum exposure of the sample surfaces for the extraction. The addition of anhydrous sodium sulfate to the sample (1:1) may make the mixture amenable to grinding.

14.12.4 Extraction method for samples expected to contain low concentrations of organics (less than or equal to 20 mg/kg):

14.12.5 The following steps should be performed rapidly to avoid loss of the more volatile extractables.

14.12.6 Weigh approximately 25 g of sample into a 400-mL beaker. Record the weight to the nearest 0.1 g.

14.12.7 Nonporous or wet samples (gummy or clay type) that do not have a free-flowing sandy texture must be mixed with 60 g of anhydrous sodium sulfate, using a spatula. If required, more sodium sulfate may be added. After addition of sodium sulfate, the sample should be free flowing.

(NOTE: In order for the sonication extraction to work properly, the sample <u>MUST</u> be dry and free flowing. If the material cannot be poured like sand through an hourglass, then the sample is not considered dry and free flowing.)

14.12.8 Add 1.0 mL of the surrogate standard solution to all samples, spiked samples, QC samples, and blanks.

14.12.9 For the sample in each batch selected for spiking, add 1.0 mL of the matrix spiking solution.

14.12.10 Immediately add 60 mL of the appropriate/recommended extraction solvent or solvent mixture (see Appendix 1).

14.12.11 Place the beaker containing the sample into the sonicator water bath.

14.12.12 Extract ultrasonically for 3 minutes, with output control knob set at 10 (full power) and with mode switch on Pulse (pulsing energy rather than continuous energy) and percent-duty cycle knob set at 50% (energy on 50% of time and off 50% of time).

14.12.13 Decant the extract and filter it through a glass powder-funnel that is attached to a clean 300-mL Zymark tube. The funnel should be filled with sodium sulfate and silica gel as listed in section 14.11.14 below. Be sure there is enough glass wool in the funnel to prevent any solid portions from entering the Zymark tube.

Repeat the extraction two more times with each extraction adding 60 mL portions of solvent. Decant off the solvent after each ultrasonic extraction. The number of extractions can be increased beyond 3 if the sample is suspected to be difficult to extract and would yield more hydrocarbons with further extraction.

14.12.14 Silica gel Cleanup (**mandatory**)

14.12.14.1 The silica gel cleanup is performed by creating a drying column by plugging a glass funnel with glass wool or inserting a #4 Whatman filter paper then filling the funnel with some silica gel then anhydrous sodium sulfate creating a large top layer of sodium sulfate and smaller bottom layer of silica gel. The entire amount of extract is filtered through this drying column then concentrated to1mL as outlined in section 14.10.

14.12.14.2 Transfer cleaned extract to a labeled vial with a Teflon®-lined screw cap or sealed Teflon®-lined septum vial for analysis.

14.12.15 Dilution Technique

14.12.15.1 This is used for product or waste samples, which are soluble in methylene chloride.

14.12.15.2 Weigh 1 g of sample into a 10 mL volumetric flask. Dilute to 10 mL with methylene chloride. Pass an aliquot of sample through a small (pipet) column of Na_2SO_4 to dry. Once dry, pass this aliquot through a small (pipet) column of silica gel_4 as clean-up.

14.13 Gas Chromatography

14.13.1 See front of the FID instrument in Semivolatiles for the conditions used in operating the GC.

14.13.2 Performance Criteria: GC run conditions and columns must be chosen to meet the following criteria:

14.13.2.1 Resolution of C_8 from the solvent front.

14.13.2.2 The column must be capable of separating typical petroleum hydrocarbon components from the surrogates.

14.14 Gas Chromatograph Analysis

14.14.1 Samples are analyzed by GC/FID. Injection volumes are 2 µL.

14.14.2 If an initial calibration has already been performed, verify the calibration by analysis and evaluation of a CCV on each working day.

14.14.2.1.1 In addition, a continuing calibration standard must be run every 10 samples and at the end of the sequence.

14.14.3 Evaluate the continuing calibration response. See 13.7 for evaluation criteria.

14.14.4 A methylene chloride blank (instrument blank) must be run at the beginning of every sequence to determine the area generated on normal baseline bleed under the conditions prevailing in the 24 hour period. This area is determined by continuous integration of all responses under the same conditions (i.e. forced baseline and predetermined time interval) as the standards and samples. This blank's calculated value (PHS concentration) shall be less than the method detection limit of the method. **Do not baseline subtract.**

14.14.4.1.1 Methylene chloride blanks should also be run after samples suspected of being highly concentrated to prevent carryover. If the blank analysis shows contamination, the column must be baked out and subsequent blanks analyzed until the system is shown to be free from contaminants as demonstrated with an instrument blank below detection level.

14.14.5 If the sample concentration exceeds the linear range of the method in the final extract, the extract must be diluted and reanalyzed.

14.14.6 Qualitative Identification (Pattern Recognition): - (Optional)

14.14.6.1 The laboratory may qualitatively identify the petroleum products when reporting data by direct comparison of sample chromatograms to retention times and peak patterns of pattern recognition standards. The experience of the analyst weighs heavily in the interpretation of the chromatogram.

14.14.6.2 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.

14.14.7 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, motor oil, etc.) that can be referenced in the Semivolatiles room.

14.14.8 All maintenance will be performed in a timely manner and recorded in a maintenance log designated to each GC/FID used in FL-PRO analysis. All entries in the maintenance logs will be written down explaining the maintenance performed then signed and dated by the analyst performing the maintenance, in accordance with the Quality Manual section 8.3.

14.13.8.1 Liner change- The injection liner will be changed every seventy five to one hundred injections or if the liner is suspected to be a source of contamination.

14.13.8.2 Septa change- the injection septa will be changed every fifty to sixty injections or if low carrier gas pressure indicates possible worn or degraded septa.

14.13.8.3 Temporary files- Temporary files will be deleted biweekly or sooner if the turbo Chromatography Workstation software or computer system becomes delayed or unresponsive.

14.13.8.4 Clock reset- the clock will be reset on the computer system when there is a change due to daylight savings time or due to any abnormalities. The time must be reset by the analyst and witnessed by the department supervisor.

14.13.8.5 Detector- Maintenance will be performed on the GC/FID detector when signal noise interferes with chromatography and or becomes too problematic for the analyst to accurately perform FL-PRO analysis due to distorted peaks and or baselines.

14.3.8.4 Column- the column will be replaced when chromatography degrades resulting in distorted peak shapes peak tailing, poor peak resolution and when the column becomes brittle and or worn. The front end of the column may be trimmed to eliminate contaminants that persist after other techniques have been unsuccessful.

14.3.8.5 Data files- Data files will be erased after they are six months old. Method files that are six months old will be saved to diskette.

14.3.8.6 Other maintenance- All other maintenance performed on either the GC/FID or software systems used to perform FL-PRO analysis will be performed on a “need to do basis” at the department supervisor’s discretion.

15.0 Calculations

15.1 **TRPH determination:** The integrated area for **all** peaks eluting from n-octane through n-tetracontane shall be determined using a baseline drawn from the baseline point prior to n-octane to a point past n-tetracontane where the baseline returns to normal (see Figures 1 and 2 and paragraph 2 of 9.3.1). All

area including the "hump-a-gram" and surrogate standards shall be included. **Do not** integrate valley to valley for individual peaks (except for surrogates). The concentration shall be determined by calibration factor or linear regression , and the solid samples shall be calculated to report on a dry weight basis. (Note: subtract out the surrogates from the total number when determining the final result. Determine the surrogate amount based on valley to valley integration. The surrogates are the only peaks to be integrated valley to valley.)

15.1.1 Calibration Factor:

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

Where:

Cs	=	Concentration of Petroleum Hydrocarbons (mg/L or mg/kg)
Ax	=	Response for the Petroleum Hydrocarbons in the sample (baseline to baseline integration), units in area
Ve	=	Volume of final extract (mL)
D	=	Dilution factor, if dilution was performed on he sample prior to analysis. If no dilution was made, D = 1, dimensionless
CF	=	Average Calibration Factor from **initial** calibration.
Inj	=	Volume of injected sample (µL)
Vs	=	Volume of sample extracted in mL or weight of sample in g

Surrogate determination: The surrogate standard recoveries in each sample must be calculated. Unlike the calculation of petroleum hydrocarbons, the response must be based on a valley-valley integration of the peak response. If recoveries are outside method limits, verify calculations, dilutions, standard solutions and instrument performance.

The surrogates result as calculated from the valley to valley integration shall be subtracted from the total raw result when determining the final TRPH result.

15.1.2 Linear Regression

$$Ce = A + BAx$$

Where:

Ce	=	Concentration of Petroleum Hydrocarbons in extract (µg/mL)
Ax	=	Response for the Petroleum Hydrocarbons in the sample (baseline to baseline integration), units in area
A	=	y-intercept value
B	=	Slope

$$Cs = \frac{(Ce)(Ist)(Ve)(D)}{(Inj)Vs)}$$

Where:

Cs	=	Concentration of Petroleum Hydrocarbons (mg/L or mg/kg)
Ce	=	Concentration in extract determined from linear regression (µg/mL)

Ist	=	Amount of each standard injected (µL) - must be constant for all standards
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
Inj	=	Volume of injected sample (µL)
Vs	=	Volume of sample extracted in mL or weight of sample in g

15.2Dry weight determination:

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

Where:

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

15.3 $$\%\ \text{RPD} = \frac{|\text{Difference b/w Dups}|}{\text{Average of Dups}} * 100$$

15.4 BREAKDOWN OF SPIKES AND VOLUMES USED FOR LIMS (HORIZON) ENTRY

Flopro consist of totaling all peaks on the chromatogram between C8 and C40, in other words the entire blob or "hump-a-gram". The only way to calibrate for this is to use single peaks over that range then add them together.

LCS, MS, MSD are all spiked with (17 peak mix at 25PPM each) for total spike of 425PPM. Recovery should be based on this total only.

Instrument is calibrated at instrument in PPM range from 68 ppm to 5100 ppm. (4x17 to 300x17)

Waters: 1 liter of water is spiked with **1ml** of surrogates: OTP at 50 mg/L
C39 at 300 mg/L
LCS, MS, MSd spiked with one ml of TPH TPH at 425 mg/L

This puts the concentration of the spike in the water at: OTP 50 ug/L surr.
C39 300ug/L surr.
TPH 425 ug/L

Waters: 250mls of water is spiked with **.25ml** of surrogates: OTP at 50 mg/L
C39 at 300 mg/L
LCS, MS, MSd spiked with one ml of TPH TPH at 425 mg/L

This puts the concentration of the spike in the water at: OTP 50 ug/L surr.
C39 300ug/L surr.
TPH 425 ug/L

The results shall report out of Horizon and on the final report to the client at an adjusted x4 versus when volume is extracted at 1 liter.

The Math broken out for 1000mls

$C_1 V_1 = C_2 V_2$ or $\frac{C_1 V_1}{V_2} = C_2$

where C_1 = concentration of parent standard
V_1 = volume of standard used
C_2 = final concentration of spiked volume
V_2 = final volume

Solve for C_2 for OTP

50mg/L x 1 ml = C_2 x 1000mls

$\frac{50 Mg/L \times 1 ml}{1000ml} = C_2$ $\frac{50 Mg/L \times 1 ml}{1000ml} = C_2$ $\frac{50 Mg/L}{1000} = C_2$

0.05 mg/L = 50 ug/L = C_2

To be able to read on the instrument, this 1 liter volume is concentrated to 1ml of extract. The extract is a 1/1000 concentrate, so the extract itself is 1000 times greater. The 1/1000 concentration is factored back in for a final result in ug/L when reported by Horizon.

Horizon sees the raw off the instrument as 50 mg/L.

Horizon then sees the 1/1000 concentration from the extraction entry and computes that in for a final result as 50 ug/L.

To do soils, the same math applies, but with different volumes and final units.

Soils 25 grams of soil is spiked with **1ml** of OTP at 50 mg/L surrogate
C39 at 300 mg/L surrogate
LCS-Total TPH 425 mg/L

Concentration of soil then becomes OTP at 2 mg/Kg
C30 at 12 mg/kg
LCS TPH at 17 mg/kg

The 25grams is then concentrated to 1ml of extract for analysis 1/25 concentration factor.

The Math broken out

$C_1 V_1 = C_2 V_2$ or $\frac{C_1 V_1}{V_2} = C_2$

Solve for C_2 for OTP

50mg/L x 1 ml = C_2 x 25gr or 0.025 Kg

$\frac{50mg/L \times 1\ ml}{0.025\ Kg} = C_2$ $\frac{50mg/L \times 0.001\ L}{0.025\ Kg} = C_2$ $\frac{50mg \times 0.001}{0.025\ Kg} = C_2$

$\frac{0.005\ mg}{0.025\ Kg} = C_2$ 2 mg/Kg = C_2

Again, concentration is 1/25 in solvent, so raw read off instrument is 2 x 25 = 50mg/L

Final result computed with concentration factored, so final Horizon report is 2mg/Kg

16.0 Method Performance

16.1 The initial demonstration of capability study for water needs 55-118% recovery and an RSD of 20% or less to pass. The initial demonstration of capability study for soil needs 63-153% recovery and an RSD of 25% or less to pass. The demonstration of capability are completed and documented in accordance with ADMIN-030 and Quality Manual 3.0.

16.2 A matrix spike and spike duplicate are to be extracted and analyzed every extraction batch not to exceed 20 billable samples with required recoveries listed in Appendix 2.

16.3 A laboratory control spike is to be extracted and analyzed every extraction batch not to exceed 20 billable samples with required recoveries listed in Appendix 2.

16.4 Surrogate recovery is to be monitored with acceptance limits listed in Appendix 2.

16.5 ICVs are to run whenever a curve is built, or quarterly, whichever is soonest. These recoveries are to be within +/-20% of actual spike value.

16.6 A calibration curve is to be run with the standards listed in 10.4.3. To use the standards as calibration factors and % RSD of 20% or less must be meet. To use in a curve, a first order regression must have a correlation coefficient of 0.995 or better.

16.7 The curve must be verified daily, every 10 billable samples, and at the end of the run with a Calibration Check verification standard. Response must fall within =/- 25% of true value.

16.8 If any of the above criteria are not met, do corrective action, then repeat.

17.0 Pollution Prevention

17.1 See Standard Methods section 1100, 20th Edition – Waste Minimization and Disposal.

17.2 See SOP Admin-018 and the AEL Safety Manual.

18.0 Data Assessment and acceptance criteria for quality control measures

18.1 See Appendix 2 (in section 24) and section 16.0 for acceptance limits.

18.2 See Appendix 3 (Sect 24) for out of control or unacceptable data.

19.0 Corrective actions for out of control data

19.1 See Appendix 3 (Sect 24) Acceptance/Rejection Policy for Data

20.0 Contingencies for handling out of control or unacceptable data

20.1 See Appendix 3 (section 24)

21.0 Waste Management

21.1 Refer to SOP for Waste Management (ADMIN-018) for any other questions.

21.2 See Standards Method section 1090, 20th Edition – Waste Minimization and Disposal.

22.0 Scheduled Maintenance

22.1 A regular schedule of maintenance is dictated more by the instrument checks and a visual check of the chromatography more than by any set schedule. Most maintenance is done in response to a failure of one of the QC checks done during the course of normal operation or poor chromatographic performance. These checks ensure that the instrument is working at the top of its performance and is proof that the instrument is in good working order.

22.2 The chromatography is reviewed on a daily basis. If the resolution is seen to degrade, if there is excessive peak tailing, or the peaks are seen to broaden and flatten, then anyone of these conditions may indicate the column needs replacing. This more than any set schedule should determine when the column needs replacement. On average, a column will require replacement once every one to two years, but can be much sooner dependant on sample load.

22.3 Hot or dirty samples or the cumulative effect of many samples can cause the chromatography to degrade as well. Changing the liner and/or trimming the column end can bring performance back to normal operation. However, in some cases when the chromatography is not improved with this maintenance, the column will require replacement.

22.4 A dirty detector can result with use over time. If the baseline is seen as becoming erratic or the signal response is seen to degrade, this may indicate that the detector needs cleaning. Slightly sanding down the contacts and cleaning the flame jet will most times restore full signal. However, if the background remains erratic or the signal remains weak, this may be an indication that a new flame jet is needed.

22.5 Failure of the FID detector to light is also an indication that the flame jet may need cleaning. If the detector still continues to fail to light even after cleaning, then the balance of hydrogen and air may need adjustment. Any adjustment to the gases will require a new curve.

22.6 A degradation of the late eluting peaks and poor performance of C-39 may be an indication of the analytes precipitating out of solution or an indication of too low a detector

temperature. If the heater at the detector is becoming weak or failing, the first indication will be the seen in the late eluting peaks.

22.7 The following maintenance list below will be placed in the maintenance logbooks. The time frames below represent the average at which this maintenance is normally performed, however this maintenance will be performed at shorter intervals or longer intervals, dependent upon the actual working state of the instrument.

Instrument Preventative Maintenance Schedule – FID

*Daily:
-Keep wash/rinse vials filled with appropriate solvent

*Weekly:
-Check CCV results to see if a liner or septa change is needed and perform if so
-Check sealant o-ring when replacing liner and replace if needed

*Monthly:
-Clean autosamplers and check that needles are clean and in working condition (clean or replace if needed)

*Quarterly:
-Run New Calibration Curve

***NOTE:
The appearance of the chromatography, peaks shape, etc. as well as background drift will also indicate a requirement for maintenance such as replacing the column, liners, septas, o-rings etc.

Air tank pressure should be consistently checked and tanks should be replaced as needed. Any instrument maintenance that is performed is to be recorded in the instrument-appropriate maintenance log.

23.0 References

23.1 Method for Determination of Petroleum Range Organics (Method #FL-PRO) Revision 1, Nov 1,1995 Florida Department of Environmental Protection
23.2 AEL Quality Manual
23.3 Standards Method section 1090, 21st Edition
23.4 AEL Admin SOPs

24.0 Appendices, Diagrams, flowcharts, and validation data

24.1 Validation Data. See the employee file for the following individuals for an acceptable initial demonstration of capability, which serves as validation date for this method in AEL.

24.1.1 Jacksonville: Brad Plummer, Travis Heal
24.1.2 Tampa: Jonathan Nuesca, Natalie Tafuni
24.1.3 Miami: Georgene Johnson

24.2 **Appendix 1**

Components in Petroleum Hydrocarbon Standard

Octane (C_8)
Decane (C_{10})
Dodecane (C_{12})
Tetradecane (C_{14})
Hexadecane (C_{16})
Octadecane (C_{18})
Eicosane (C_{20})
Docosane (C_{22})
Tetracosane (C_{24})
Hexacosane (C_{26})
Octacosane (C_{28})
Triacontane (C_{30})
Dotriacontane (C_{32})
Tetratriacontane (C_{34})
Hexatriacontane (C_{36})
Octatriacontane (C_{38})
Tetracontane (C_{40})

24.3 **Appendix 2**

Method Acceptance Criteria Table

Sample Type	Percent Recovery in Water	Percent Recovery by Soxhlet	Percent Recovery by Soil Sonication	Precision (%RSD) in Water	Precision by Soxhlet	Precision by Soil Sonication
Samples	41-101	41-224	62-204	0-20	0-25	0-25
Laboratory Control Samples	55-118	63-135	63-153	0-20	0-25	0-25
Surrogate OTP	82-142	57-115	62-109	NA	NA	NA
Surrogate C_{39}	42-193	61-153	60-118	NA	NA	NA

24.4 Appendix 3

Acceptance Rejection Policy for Data Generators in the Organics Department

- Instrument must be clean as exhibited by an instrument blank at the beginning of each analytical batch.
- Each analytical batch at a minimum will follow the "12 hour rule". This being a CCV and where applicable.
- The CCV must meet method acceptance criteria to report unqualified data. If any analyte fails with a low recovery, no data results can be reported for that analyte. If any analyte fails with a high recovery,

no detects can be reported if qualified. Corrective action (remixing standard, cleaning injection liner, etc.) Should be taken before next analytical batch.

- Laboratory Control Spikes must fall within control chart limits for percent recoveries of both analytes and surrogates for valid data reporting. If it fails, check instrument first for possible problems-document-then re-shoot LCS. If it still fails, then all samples in the extraction batch must be re-extracted or reanalyzed. At this point notify your supervisor. If unable to re-extract, NCF must be generated and the lab manager notified. (QA officer will be notified in writing with the NCF)
    - NOTE: LCS and MB must meet all recovery requirements to show the extraction (or purge) process is viable. If a trend is seen to develop thru the analytical batch and can be corrected by instrument procedures (recalibrating, cleaning, etc.) then this should be done. The analyst should document this fully on the data packet cover sheet. An example of this would be a CCV that just falls inside limits on the low side with a LCS (slightly weaker thru the extraction process) falls outside the limits low. Obviously the curve was pushed too far. The analyst should maintain operating conditions and curves so that this is not a common occurrence.

- Matrix spike/Spike Duplicate-Failure to meet control limits for analyte and surrogate recoveries does not in itself require data to be rejected. Data will be flagged (J4) for matrix interference.

- Method Blank-Must pass surrogate recovery acceptance limits and is clean of analytes of interest. If there are hits on the method blank, these hits should be below the method reporting level. If the hits are above the method reporting level, and the samples themselves are clean of those hits, the samples results are fine to report out. If above the MRL, and samples have the same hits- then sample results will not be accurate and the method blank must be re-shoot and /or re-extracted to prove that the hits were not contamination.

- At any point in the analytical batch, an analyst may use his/her discretion to fail or reject data he/she feels to be suspicious or in error. At this point, the analyst will seek the help of a supervisor or the QC officer.

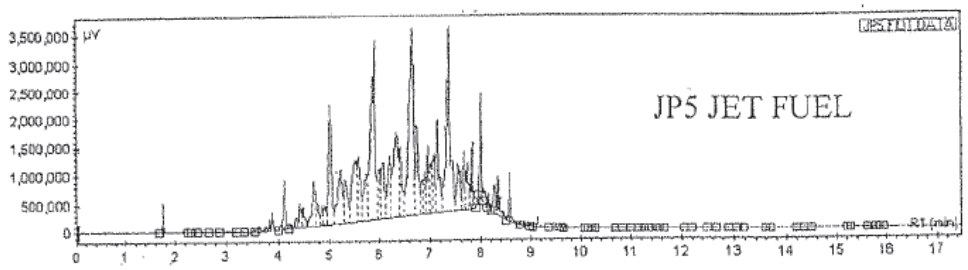
- Data will be rejected for individual sample runs if the chromatogram looks odd, times shift outside retention time windows, or surrogates fail due to reasons other than matrix interferences.

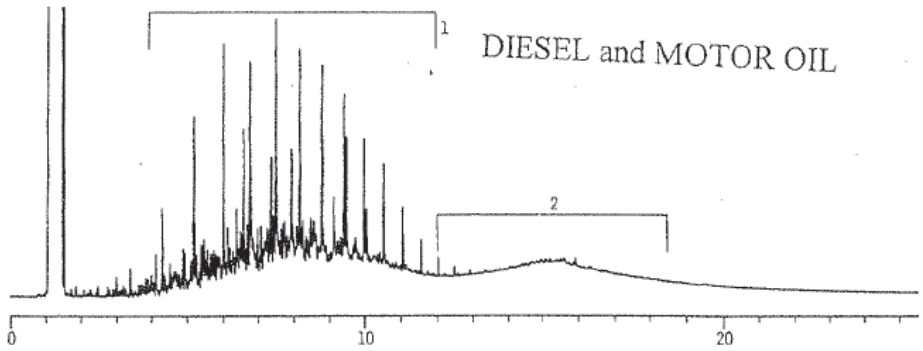
- For external calibration instruments-A closing CCV must finish out the analytical batch. See earlier reference to CCVs.

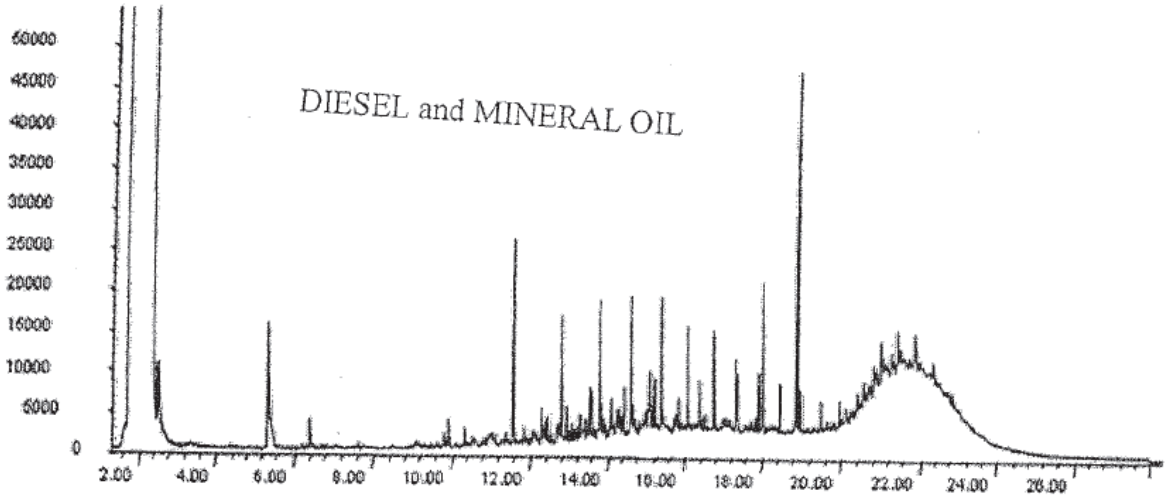
- Any and all QC failures must be reported to a supervisor and the QC officer.

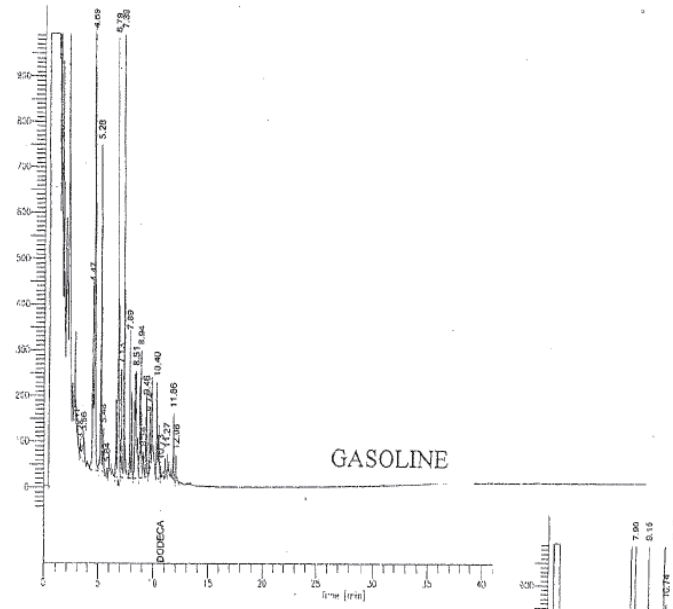
- Extraction personnel will be informed of any failures immediately. They will also be informed of any trends that develop in sample recoveries.

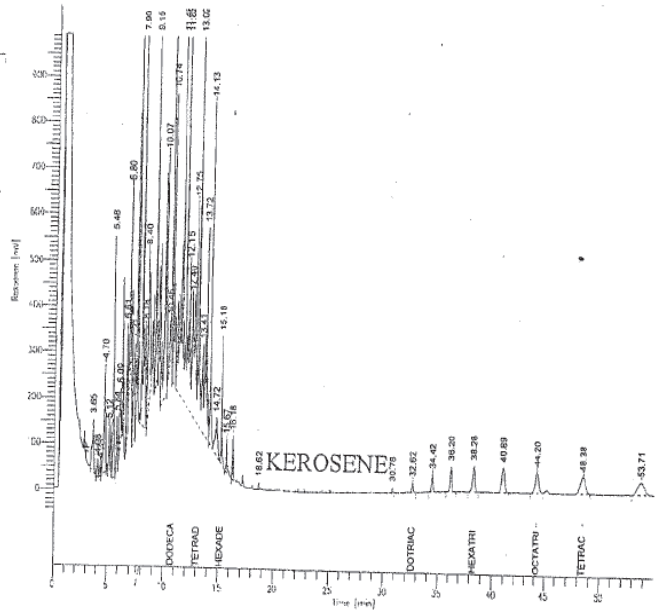
24.5 **Appendix 4** Example Chromatograms for Identifying Petroleum Products

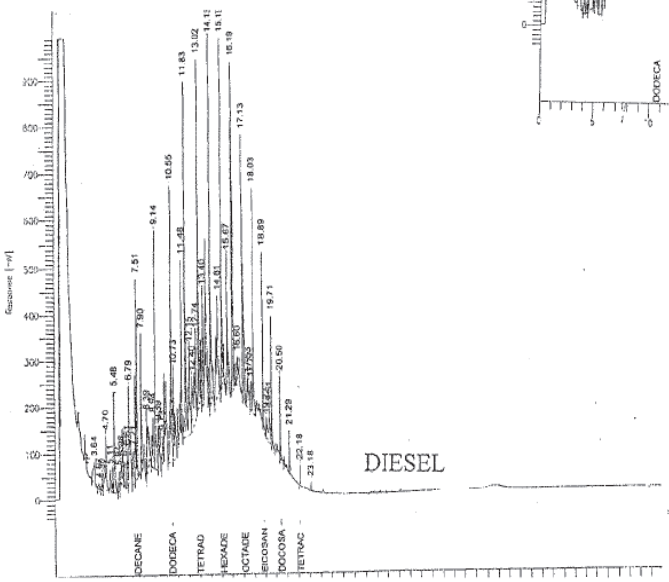

JP5 JET FUEL

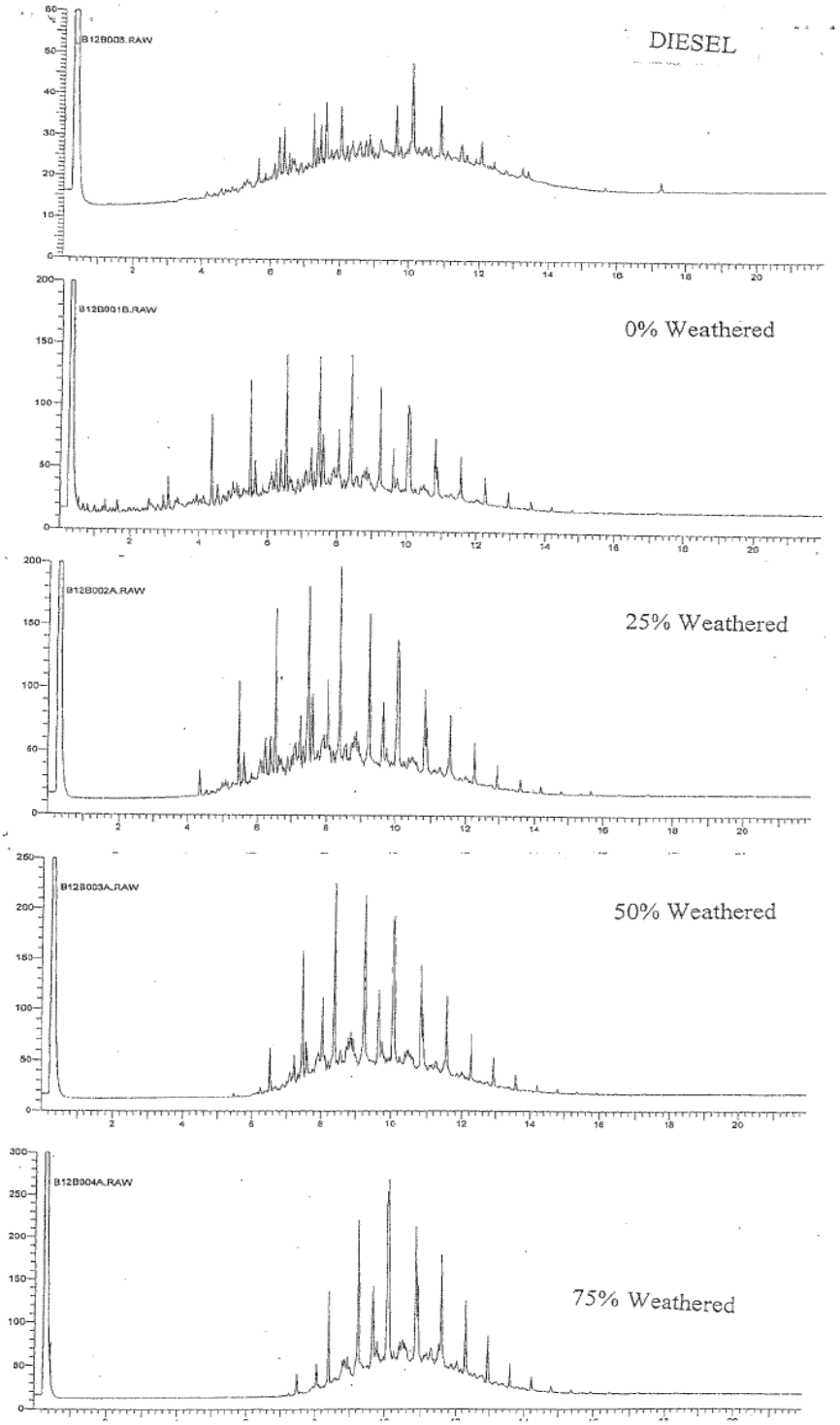

DIESEL and MOTOR OIL
1
2


DIESEL and MINERAL OIL


GASOLINE
DODECA


KEROSENE
DODECA
TETRAD
HEXADE
DOTRIAC
HEXATRI
OCTATRI
TETRAC


DIESEL
DECANE
DODECA
TETRAD
HEXADE
OCTADE
EICOSAN
DOCOSA
TETRAC


B12B003.RAW
DIESEL
B12B001B.RAW
0% Weathered
B12B002A.RAW
25% Weathered
B12B003A.RAW
50% Weathered
B12B004A.RAW
75% Weathered

24.6 Appendix 5 Ranges of Common Petroleum Products

Number of Carbons Composing Common Petroleum Products

Product	**Number of Carbons**
V.M.&P.	6-10
Mineral Spirits	8-10
Gasoline	4-13
Kerosene	8-17
#2 Diesel	11-20
JPS, Jet Fuel	10-16
Heavy Oil	15-24
Gas Oil, Fuel Oil	11-28

Carbon range in petroleum hydrocarbons generally indicates the boiling point or volatility of a particular product. Petroleum hydrocarbons containing from six to eight carbons usually contain aromatic (BTEX) components.