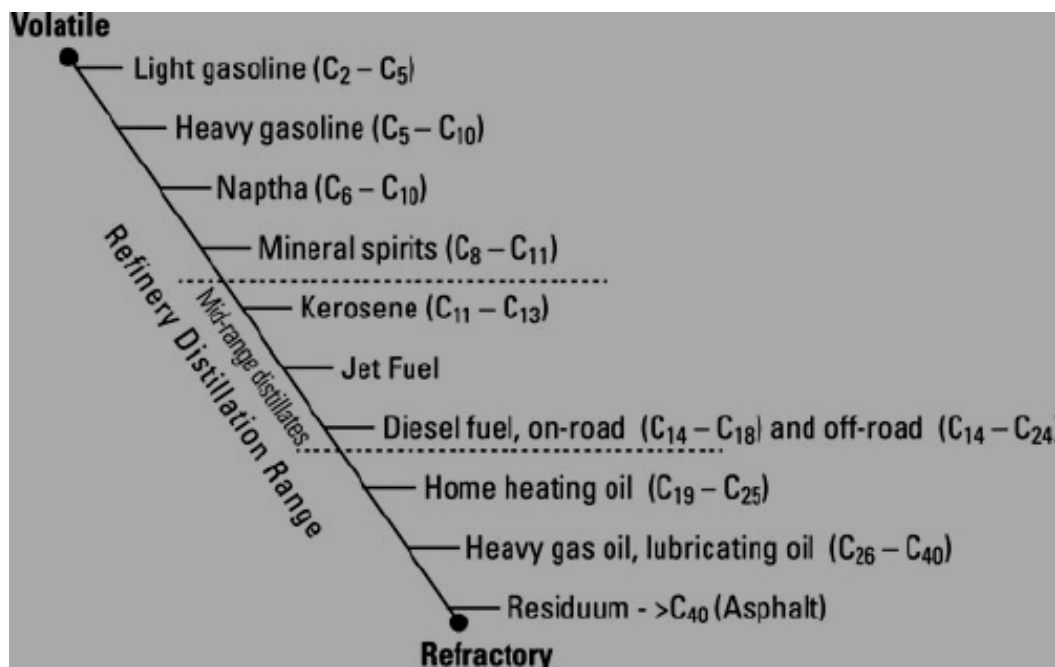


STANDARD OPERATING PROCEDURE

For

FL-PRO
2018

DETERMINATION OF PETROLEUM RANGE ORGANICS





SOP Revision Log for AEL SOP SVOC-004

Revision Number	Revision Date	Reason for Revision	Section(s) and Page(s) Revised
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 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 analysts in section 23, iDOC performance	Sections 10 and 23
Revision 05	5/15/10	Re-write of section 1, expanded sections 6, 13 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 spike and final volumes are in use. Section 14.2 thru 14.10, reworded procedure to mark bottles and wait until after extraction to measure volume. Sample taken directly from bottle, with bottle being rinsed with solvent. Section 9.17 column in use is 30 meters.	Sections 1, 9, 14
Revision 07	8/27/15	Reviewed with no changes. FDEP review and approval for volume at 250 (initially for 3/28/15 rev, but again for Tampa and Miami 8/21/15)	no changes
Revision 08	9/18/15	C39 surrogate concentration set at 150 ug/L from 300 ug/L. Surrogates can be constant in the curve.	Sections 1.2, 10.7, 13.2, 14.5, 15
Revision 09	9/15/17	Expand calibration procedures to include weighted linear regression. Adjustment of the calibration curve concentrations and initial sample volume in the method summary. Add procedure for using final extract for both FL-PRO and PAH analysis when adding PAH surrogates prior to extraction. Updated the method validating analysts.	Sections 1.2, 1.4, 5.0, 10.7.2, 13.0, 13.4, 14.5,14.12.8, 14.13.2, and 24.1
Revision 10	4/30/19	Update procedures and QC to 11/2/2018 rev. Update references. QC Limits updated in sections and tables.	All sections affected
Revision 11	1/13/21	Update to read CCV every 10 billable samples. Update MDL procedure. Include rules for relative error and its calculation. Update references. Update validating analysts.	Sections 12.9, 12.14, 13, 23, 24



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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 11/2/2018 Florida Department of Environmental Protection in the following areas: Standards are all purchased from certified vendors and are not made from stock reference materials. Surrogates are spiked with 1.0 mL 50 µg/mL OTP and 150 µg/mL C39 instead of 2mL of 100 µg/mL each OTP and C39. Initial Calibration is performed using 6 concentration levels at 10, 20, 50, 100, 250 and 500 µg/mL of each C8-C40 even-numbered alkane versus the suggested concentration levels at 5, 25, 50, 100, 200, and 300 µg/mL. This is equivalent to 170, 340, 850, 1700, 4250, and 8500 µg/mL total alkanes in the standards. Extractions on soils are done ultrasonically in sonication baths. 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 Method FL-PRO Revision 11/2/2018 in that it allows for a smaller sample volume of 250mL versus the method listed volume of 1000mL 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.
- 1.4 This SOP also allows for the use of a single sample container for the extraction and analysis of under both FL-PRO and PAH 8270 SIM methods. All samples would require acid preservation and all samples and QC would be spiked with both FL-PRO and PAH SIM surrogates.

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 C₈ - C₄₀.
- 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.

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 ne product. See tables at the end of this SOP for some illustrations of fingerprint patterns.

5.0 Summary of Method

- 5.1 250mL or 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 SW-846 test methods. Refer to the original test method's reference section (FDEP Determination of Petroleum-Range Organics Method FL-PRO, section 14) for a full listing of materials on which this method is based.
- 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 this SOP's 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-C₈) and the peak end after n-tetracontane (n-C₄₀). 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 C₈ to C₄₀ (Table 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) – An analyte-free matrix to which all reagents are added in the same volumes or proportions as used in sample processing. The method blank is carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.
- 6.6
- 6.7 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.
- 6.8 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 its 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



- 6.9 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.
- 6.10 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.
- 6.11 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.
- 6.12 Stock Standard -- A concentrated solution containing method analytes that is purchased from a commercial source having Certificates of Analysis.
- 6.13 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.
- 6.14 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.
- 6.15 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.
- 6.16 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.
- 6.17 Safety Data Sheets (SDS): 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. A typical batch of 20 samples could be IB, CCV, MB, LCS, MS, MSD, samples 1-10, CCV, IB, samples 11-20, closing CCV.
- 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 if 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
 - FL Failed Low
 - FH Failed High
 - CF Confirmation
 - DIL Dilution
 - DF Dilution Factor
 - STD Standard
 - STR Straight/No Dilution
 - SURR Surrogate
 - IS Internal Standard
 - WRT Wrong Retention Time
 - DNR Do Not Report



BDL Below Detection Limit
IS/SURR Internal Standard/Surrogate
INT STD Intermediate Standard
WS Working 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, 22nd 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 (C₃₉). A working solution is made at 50 µg/mL (OTP) and 150 µg/mL (C₃₉) 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 PAH SIM Surrogates: When the sample extract is to be used for both FL-PRO and PAH SIM analysis, the PAH SIMs surrogate will be added to the sample so as to obtain a 5 ug/L final concentration. A working standard is made at 5ug/ml in acetone with 1ml spiked into each sample prior to extraction.

10.7.3 Individual stock solutions of C₈ - C₄₀ even normal alkanes (see Table 1). For solubility reasons, it is necessary to prepare stock solutions of n-alkanes in solvents of acetone and carbon disulfide.

10.7.4 Petroleum Hydrocarbon Standard: C₈ - C₄₀ even normal alkane standards with each component at 2000 µg/mL. Calibration levels are mixed from this stock standard solution at levels of 10, 20, 50, 100, 250, and 500 µg/mL of each individual component. This is equivalent to 170, 340, 850, 1700, 4250, 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.

10.7.5 Silica gel

10.7.5.1 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. See also AEL Admin-005 and Admin-023

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



11.3 The samples must be stored at $\leq 6^{\circ}\text{C}$ from the time of collection until extraction. Do not freeze samples. Samples hand-delivered to the laboratory on the day of sample collection and received in wet ice may not have equilibrated to the required preservation temperature by the time of receipt. This would not be considered an anomaly and those samples would not require qualification.

11.4 Extraction must be performed on waters within 7 days of sample collection and on soils or wastes within 14 days of sample collection. Sample extracts must be stored at $\leq 6^{\circ}\text{C}$. All analyses must take place within 40 days of extraction.

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 66-119% recovery and an RSD of 20% or less to pass. The initial demonstration of capability study for soil needs 65-119% 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 laboratory control sample (LCS), matrix spike (MS) sample and matrix spike duplicate (MSD) sample or (LCS duplicate in place of and MSD) 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 (also referred to as CCV) must be analyzed every 10 billable samples or every 12 hours, whichever is soonest. 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, 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.

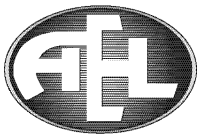
12.11.4 Low recoveries may also be caused by incorrect integration. The chromatographic profile of motor oils does not give baseline resolution of all components, resulting in a characteristic rise in baseline underneath the resolved hydrocarbon components known as the "unresolved complex mixture", or 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 Table3 (Sect. 23.3).

12.12 The extraction volumes and solvent volumes can be adjusted away from base method listing of one liter and 60mls if new volumes are demonstrated to be equivalent in performance, qualitatively and quantitatively, with these base method volumes. Documentation, at a



minimum, shall consist of a passing Initial Demonstration of Capability using the modified volumes (see table 2). Also, all ongoing quality control requirements must be maintained while using the modified volumes. Data produced by the modified method must be equivalent to data generated using the initial procedures of the FDEP FL-PRO method.

12.13 Retention Time windows must be established. Retention Time windows must be verified each working day. See section 13.8 for a full explanation of requirements.

12.14 Method Detection Limit (MDL) - MDLs must be established for all analytes, following the procedures outlined in ADMIN SOP-012, which conforms to EPA CFR 40 part 136.6 appendix B, updated October 2017. Below is a summary of the steps for performing MDLs. Please refer to the ADMIN SOP-012 for the full procedures.

12.14.1 New MDL Study: Most MDL determinations are for already established analyte, matrix, and instrument combinations. In those cases where a new analyte is to be introduced, an initial MDL study will have to be implemented. Select a spiking level, typically 2 to 10 times the estimated MDL. Process a minimum of seven spiked samples and seven method blank samples through all steps of the method. The samples used for the MDL must be prepared in at least three batches on three separate calendar dates and analyzed on three separate calendar dates. (Preparation and analysis may be on the same day.)

12.14.2 New Instrument: To bring on a new instrument for an already established method a full set of seven low-level replicates is not needed. Only two spiked samples and two method blank samples prepared and analyzed on different calendar dates are required for the new instrument. The resulting values shall be compared against existing MDLs for validity. If both method blank results are below the existing MDL, then the existing MDL is validated. Combine the new spiked sample results to the existing spiked sample results and recalculate the MDLs. If the recalculated MDLs is within 0.5 to 2.0 times the existing MDL and fewer than 3% of the MB have results above the existing MDL, the existing MDL can be left unchanged and the new instrument is validated.

12.14.3 Existing Instrument, Major Maintenance: Follow the procedures for bringing on a new instrument.

12.14.4 Ongoing Data Collection: During any quarter in which samples are being analyzed, prepare, and analyze a minimum of two spiked samples on each instrument, in separate batches (separate prep batches and separate analytical batches), using the same spiking concentration used with established MDLs. If any analytes are repeatedly not detected in the quarterly spiked sample analyses, or do not meet the qualitative identification criteria of the method then this is an indication that the spiking level is not high enough and should be adjusted upward. Note that it is not necessary to analyze additional method blanks together with the spiked samples; the method blank population should include all of the routine method blanks analyzed with each batch during the course of sample analysis.

12.14.4.1 At least once per year, re-evaluate the spiking level. If more than 5% of the spiked samples do not return positive numerical results that meet all method qualitative identification criteria, then the spiking level



must be increased and the initial MDL re-determined following the procedure for establishing a new MDL.

12.14.5 Ongoing Annual Verification: At least once every thirteen months, re-calculate MDLs and MDLb from the collected spiked samples and method blank results using the equations in the ADMIN SOP-012. These calculations shall be performed by the QA department along with updating and maintaining all chart and LIMs entry of any MDL changes.

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. Orthoterphenyl (OTP) Surrogate Standard is at 10000 ug/mL.
- D. Nonatricontane (C39) Surrogate Standard is at 3000 ug/mL.

Intermediate standards for Surrogates

- E. 1000 mg/L OTP = 100uL of 10,000 mg/L OTP (C.) + 900uL Methylene Chloride (MECL)

FL-PRO CURVE:

ICAL (ug/mL) TRPH Final Concentration	Amount Primary Stock Std (A) to use	Amount OTP WS (C) to use	Amount C39 Stock Std (D) to use	Final Volume (DCM)
ICAL 1 (10ppm)	5uL	50uL	50uL	1.0mL
ICAL 2 (20ppm)	10uL	50uL	50uL	1.0mL
ICAL 3 (50ppm)	25uL	50uL	50uL	1.0mL
ICAL 4 (100ppm)	50uL	50uL	50uL	1.0mL
ICAL 5 (250ppm)	125uL	50uL	50uL	1.0mL
ICAL 6 (500ppm)	250uL	50uL	50uL	1.0mL
ICV (ug/mL) TRPH Final Concentration	Amount Secondary Stock Std (B) to use	Amount OTP WS (C) to use	Amount C39 Stock Std (D) to use	Final Volume (DCM)
ICV (100ppm)	50uL	50uL	50uL	1.0mL

**The final concentration of OTP is 50ug/mL and C39 is 150ug/mL.



- 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 C₈ to a point past C₄₀ 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.

13.4.1 A linear least squares regression attempts to construct a linear equation of the form,

$$y = ax + b$$

by minimizing the sum of squared differences between the observed response (y_i , the instrument response) and the predicted response (y'_i , the response calculated from the constructed equation) at each calibration level.

- 13.4.2 Weighting the sum of the squares of the differences may significantly improve the ability of the least squares regression to fit the linear model to the data, especially at the low end of the calibration curve. The general form of the sum of the squares of the differences containing the weighting factor is:

where:

$$\sum_{i=1}^n w_i (y_i - y'_i)^2$$

W_i = Weighting factor for the i th calibration standard ($w=1$ for unweighted least squares regression, or $1/x$ or $1/x^2$ for weighted least squares regression)

y_i = Observed instrument response for the i th calibration standard.

y'_i = Predicted (or calculated) response for the i th calibration standard.

n = Total number of calibration points

- 13.4.3 A weighted linear regression is set in the processing software by selecting either $1/X$ or $1/X^2$ in the weighting field within the calibration module. Since curve weighting affects the intercept of the calibration curve, whether the $1/X$ or $1/X^2$ weighting is used will be based on the analyst's discretion regarding the goodness of fit of the



calibration curve. The weighted linear regression must meet the $r^2 > 0.990$ criteria to be valid (0.995 squared).

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 for the **ICV shall be within $\pm 25\%$ (20% for DoD work)** 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 standards varies from the predicted response by more **than $\pm 25\%$ (20% for DoD work)** 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 through C_{40} shall be within the established range as determined in an initial retention time window study. This study on file in the Semi-volatiles room and be readily accessible. Compare the starting CCV times (or mid-point calibration standard if on day of calibration) to that of the study. 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, adjust the windows in the peak integration program to properly account for the shift. (See AEL SOP-TECH-010 for procedures on "Establishing and Maintaining Retention Time Windows".)

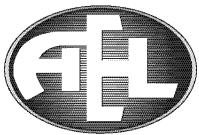
13.8.1 Before establishing windows, be certain that the GC system is within optimum operating conditions. Make three injections of the method standard throughout the course of a 72-hour period. Serial injections over less than a 72-hour period result in retention time windows that are too tight.

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

13.8.2.1 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.

13.8.2.2 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.

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



13.9 Relative Error. From the 2016 TNI Standards, the laboratory is required to use and document a measure of relative error in the calibration. By employing relative error acceptance criteria, concentrations calculated from the low end of the curve shall have the same confidence in their accuracy as those taken from any other point on the curve. Acceptance criteria must be met.

13.9.1 For calibrations evaluated using an average response factor, the determination of the relative standard deviation (RSD) is the measure of the relative error. If the average response factor acceptance criteria have been met, then acceptance is also met for the relative error.

13.9.2 For calibrations evaluated using correlation coefficient or coefficient of determination, the laboratory shall evaluate relative error by either the measurement of the Relative Error (%RE) or the measurement of the Relative Standard Error (%RSE)

Relative error is calculated using the following equation:

$$\% \text{ Relative Error} = \frac{x'_i - x_i}{x_i} \times 100$$

x_i = True value for the calibration standard

x'_i = Measured concentration of the calibration standard

13.9.3 This calculation shall be performed for two (2) calibration levels: the standard at or near the mid-point of the initial calibration and the standard at the lowest level.

13.9.4 The ICV can be used to satisfy the midpoint verification using the acceptance criteria already in place. The low level of the curve can be either recalculated for recovery as if run as an LCS, or a low level standard is to be analyzed. The acceptance criteria for the low level will be +/- 25% of true value.

14.0 Procedure

14.1 Sample preparation—Water Matrix—Separatory 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 be same amounts as listed in 14.6 through 14.9 (Note: see section 12.12 for changes in solvent volume and requirement of internal lab studies).



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 150 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

Note: When the sample extract is to be used for both FL-PRO and PAH SIM analysis, the PAH SIMs surrogate will be added to the sample so as to obtain a 5 ug/L final concentration. A working standard is made at 5ug/ml in acetone with 1ml spiked into each sample prior to extraction.

14.6 Use 60 mL of methylene chloride to rinse the bottle and transfer this rinse solvent to the separatory funnel. If hand shaking, shake the funnels at an even pace (approximately twice per second) for 2 minutes.

14.7 If using a shaker(s) 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 the setting with the best agitation without having the separatory funnels becoming dislodged or otherwise disadvantaged. If using more than one shaker, make sure the timing of the shakes is consistent throughout all the shakers used.

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 Place funnels in a ring stand. 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.

14.9 Drain the solvent layer from the separatory funnel 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.

14.10 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 in the Zymark.

14.11 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.

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

14.12.1 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. This is normally at 45°C. 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

14.12.2 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 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.

14.12.3 Place the Zymark tube containing the sample extract in the Turbo-Vap. It 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.

14.12.4 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.

14.12.5 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.

14.12.6 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.

14.13 Soil preparation – Sonication



- 14.13.1 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. (Unless otherwise dictated by the client. Note any changes to normal procedure in the comments column of the extraction log)
- 14.13.2 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.
- 14.13.3 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.
- 14.13.4 Extraction method for samples expected to contain low concentrations of organics (less than or equal to 20 mg/kg):
- 14.13.5 The following steps should be performed rapidly to avoid loss of the more volatile extractables.
- 14.13.6 Weigh approximately 25 g of sample into a 400-mL beaker. Record the weight to the nearest 0.1 g.
- 14.13.7 Nonporous or wet samples 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. Gummy or clay type soils may need much mixing until free flowing.
- (NOTE: In order for the sonication extraction to work properly, the sample MUST 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.)**
- 14.13.8 Add 1.0 mL of the surrogate standard solution to all samples, spiked samples, QC samples, and blanks. (See also 14.5 if extract is to be used for PAH analysis)
- 14.13.9 For the sample in each batch selected for spiking, add 1.0 mL of the matrix spiking solution.
- 14.13.10 Immediately add 60 mL of the appropriate/recommended extraction solvent or solvent mixture (see Table 1).
- 14.13.11 Place the beaker containing the sample into the sonicator water bath.
- 14.13.12 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).
- 14.13.13 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.

14.14 Silica gel Cleanup (**mandatory**)

14.14.1 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 to 1 mL as outlined in section 14.10.

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

Note: If the sample extract is to be used for both FL-PRO and PAH SIM analysis, the sample extract shall first be analyzed under the FL-PRO method with the internal standards needed for PAH analysis added only after all FL-PRO analysis is completed.

In the event that immediate analysis is needed under both methods, the extract shall be divided equally into two 500 µL aliquots prior to analysis, with only the aliquot for PAH analysis receiving PAH SIM internals. At these volumes, vial inserts or narrow bore vials should be used to ensure that the autosampler syringe uptakes the sample properly.

14.15 Dilution Technique

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

14.15.1.2 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 Na₂SO₄ to dry. Once dry, pass this aliquot through a small (pipet) column of silica gel₄ as clean-up.

14.16 Gas Chromatography

14.16.1 Refer to the save operating program in Semivolatiles for the conditions used in operating the GC.

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

14.16.2.1 Resolution of C₈ from the solvent front.

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



14.17 Gas Chromatograph Analysis

14.17.1 Samples are analyzed by GC/FID. Injection volumes are 2 μ L.

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

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

14.17.3 Evaluate the continuing calibration response as listed in Section 13.

14.17.4 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.**

14.17.4.1.1 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.

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

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

14.17.6.1 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.

14.17.6.2 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.

14.17.7 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.



14.17.8 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

15.1TRPH 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 the 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

$$Ce = A + B Ax$$

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)



V_s = Volume of sample extracted in mL or weight of sample in g

15.2 Dry weight determination:

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

Where:

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

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

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

FLO-PRO consists 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 50PPM each) for total spike of 850PPM. Recovery should be based on this total only.

Instrument is calibrated at instrument in PPM range from 170 ppm (10ppm x 17) to 8500 ppm (500ppm * 17).

Waters: 1 liter of water is spiked with **1.0mL** of surrogates: OTP at 50 mg/L
C39 at 150 mg/L
LCS, MS, MSD spiked with 1.0mL of TPH TPH at 850 mg/L

This puts the concentration of the spike in the water at: OTP 50 ug/L (Surr)
C39 150 ug/L (Surr)
TPH 850 ug/L

Waters: 250mls of water is spiked with **1.0mL** of surrogates: OTP at 50 mg/L
C39 at 150 mg/L
LCS, MS, MSD spiked with 1.0mL of TPH TPH at 850 mg/L

This puts the concentration of the spike in the water at : OTP 50 ug/L (Surr)
C39 150 ug/L (Surr)
TPH 850 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



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

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

$$50\text{mg/L} \times 1 \text{ ml} = C_2 \times 1000\text{mls}$$

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

$$0.05 \text{ mg/L} = 50 \text{ ug/L} = C_2$$

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 150 mg/L surrogate
LCS-Total TPH 850 mg/L

Concentration of soil then becomes OTP at 2 mg/kg
C39 at 6 mg/kg
LCS TPH at 34 mg/kg

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

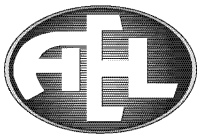
The Math broken out

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

Solve for C_2 for OTP

$$50\text{mg/L} \times 1 \text{ ml} = C_2 \times 25\text{gr or } 0.025 \text{ Kg}$$

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



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

Again, concentration is 1/25 in solvent, so raw read off instrument is $2 \times 25 = 50 \text{ mg/L}$

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

16.0 Method Performance

- 16.1 The initial demonstration of capability study for water needs 66-119% recovery and an RSD of 20% or less to pass. The initial demonstration of capability study for soil needs 65-119% 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 inside laboratory established limits as listed in table 2. (If sample volume is insufficient for an MSD extraction, an LCSD should be performed in its place.)
- 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 Table 2.
- 16.4 Surrogate recovery is to be monitored with acceptance limits listed in table 2.
- 16.5 ICVs are to run whenever a curve is built, or quarterly, whichever is soonest. These recoveries are to be within +/-25% 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 met. 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, 22nd 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 table 2 (in section 24) and section 16.0 for acceptance limits.
- 18.2 See Table 3 (Sect 24) for out of control or unacceptable data.

19.0 Corrective actions for out of control data



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

20.0 Contingencies for handling out of control or unacceptable data

20.1 See Table 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, 22nd 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 Nov 2,2018
Florida Department of Environmental Protection
- 23.2 AEL Quality Manual
- 23.3 Standards Method section 1090, 22nd Edition
- 23.4 AEL Admin SOPs
- 23.5 TNI Standards 2016
- 23.6 ISO 17025: 2005 & 2017 Standards
- 23.7 DoD ELAP QSM rev. 5.2, December 2018. and rev. 5.3 May 2019

24.0 Tables, 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 data for this method in AEL.

- 24.1.1 Jacksonville: Francis Grau Flores, Timothy Cooper
- 24.1.2 Tampa: Alyssa Henry, Anthony Buchko
- 24.1.3 Miami: Lissette Rosario, Adolfo Fernandez

See following pages for tables 1 through 5.



24.2 **Table 1**

Components in Petroleum Hydrocarbon Standard

Octane (C₈)
Decane (C₁₀)
Dodecane (C₁₂)
Tetradecane (C₁₄)
Hexadecane (C₁₆)
Octadecane (C₁₈)
Eicosane (C₂₀)
Docosane (C₂₂)
Tetracosane (C₂₄)
Hexacosane (C₂₆)
Octacosane (C₂₈)
Triacontane (C₃₀)
Dotriacontane (C₃₂)
Tetratriacontane (C₃₄)
Hexatriacontane (C₃₆)
Octatriacontane (C₃₈)
Tetracontane (C₄₀)

24.3 **Table 2**

Method Acceptance Criteria

NOTE: IDOC levels are set by base method and initial criteria. LCS and MS/MSD (Sample) levels are in-house generated limits.

% True Value

	State	DoD
CCV	25	20
ICV	25	20

% Recovery PHS

Precision (%RSD)

	Water	Soil	Waste	Water	Soil	Waste
IDOC	66-119	65-119	70-114	0-20	0-25	0-25
LCS	53-121	49-128	70-114	0-20	0-25	0-25
MS/MSD	53-121	49-128	14-197	0-20	0-25	0-25

OTP	66-139	66-136	61-138	0-20	0-25	0-25
C39	40-129	36-132	27-141	0-20	0-25	0-25



24.4 Table 3

Acceptance Rejection Policy for Data Generators in the Organics Department

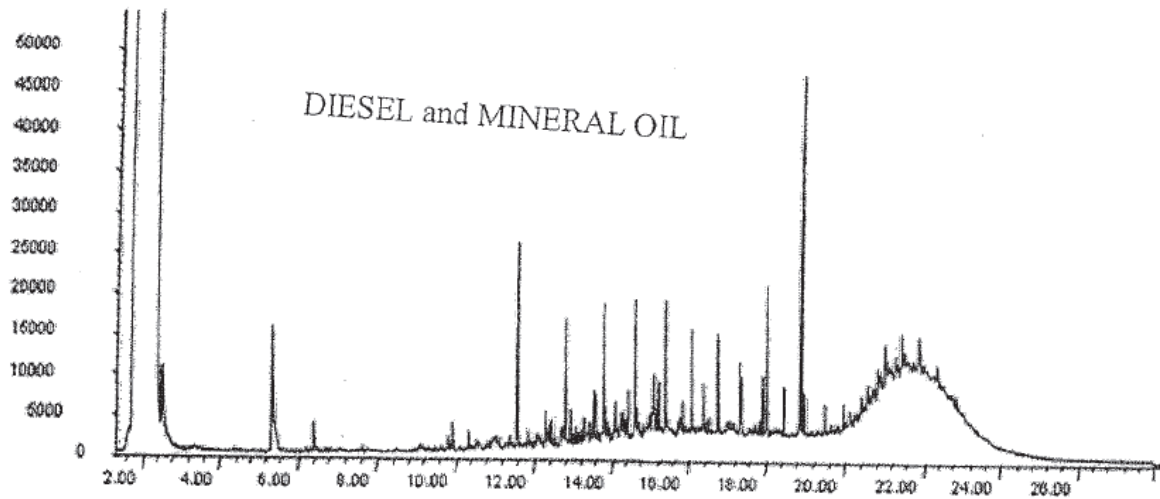
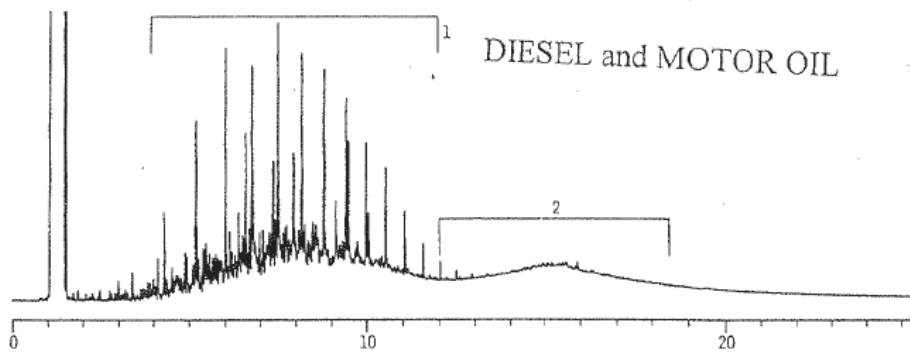
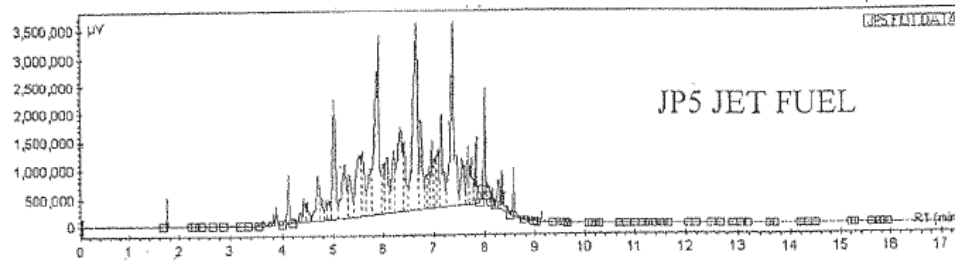
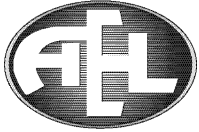
- Instrument must be clean as exhibited by an instrument blank at the beginning of each analytical batch.
- Each analytical batch at a minimum will follow the “12 hour rule”. This being a CCV and where applicable.
- The CCV must meet method acceptance criteria to report unqualified data. If any analyte 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.

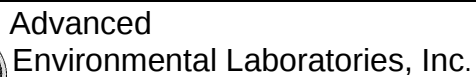


- Extraction personnel will be informed of any failures immediately. They will also be informed of any trends that develop in sample recoveries.

24.5 **Table 4:** See next page--Example Chromatograms for Identifying Petroleum Products

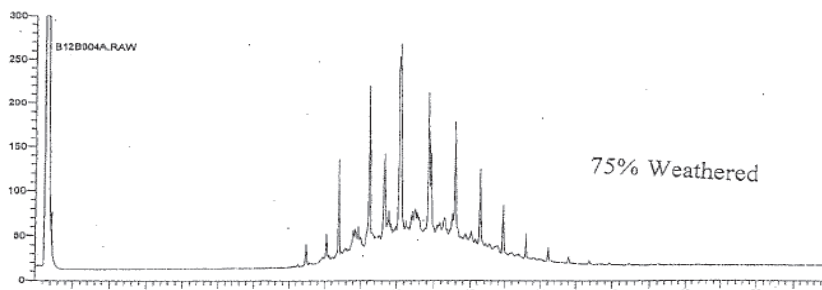
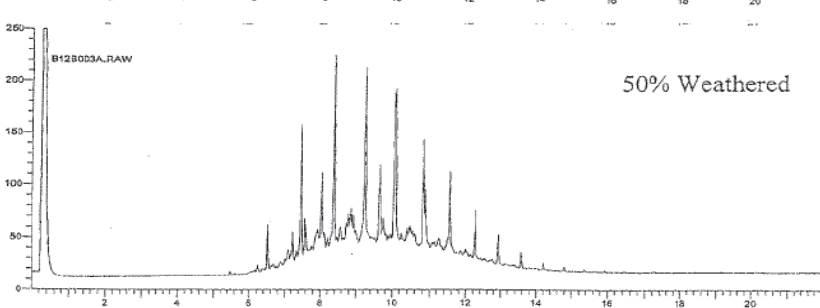
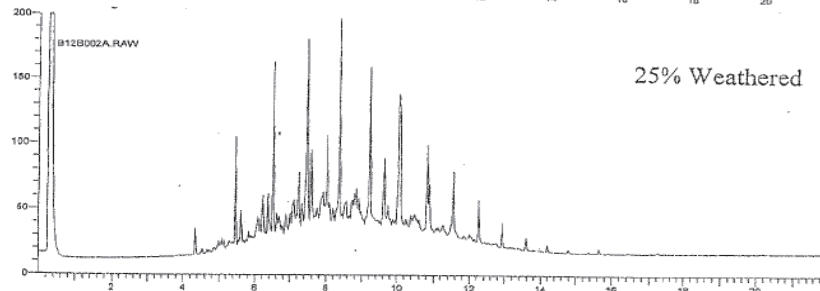
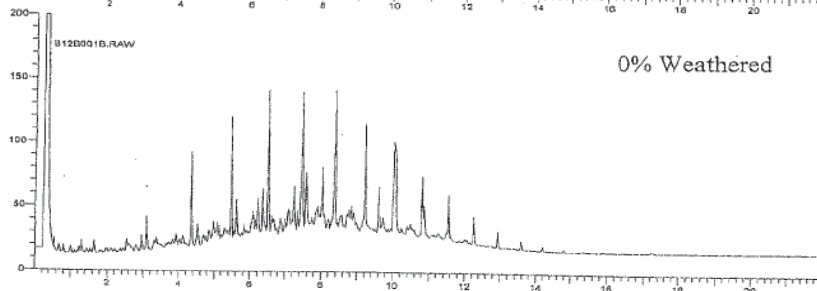
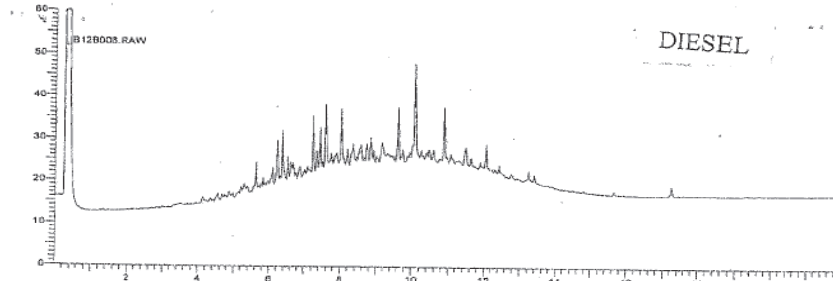
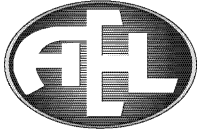
24.5 **Table 4:** Example Chromatograms for Identifying Petroleum Products





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24.6 Table 5: Ranges of Common Petroleum Products

