ESS Laboratory
Division of Thielsch Engineering
Cranston, RI

SOP 60_8100-mod
Total Petroleum Hydrocarbons
(SW846 Method 8100 modified/Conn ETPH)
BY GC/FID

REVIEWED BY:

Operations Manager	Date 6/25/08
QA Manager	Date 6/23/08
Laboratory Director	Date 6/26/08

Master marked in red. Controlled copies marked in green.

Total Petroleum Hydrocarbons
(SW846 Method 8100 modified/Conn ETPH)

1.0 SCOPE AND/OR APPLICATION

1.1 This method has been modified to determine the total petroleum hydrocarbon (TPH) content of samples from C_9-C_{36}. This range represents the major components of a number of petroleum products such as kerosene, jet and diesel fuel, No. 2 to 6 fuel oils and motor oils. Gasoline range organics are not quantitated by this method.

1.2 Compounds less than C_{36} present in products such as motor oils or lubricating oils can be quantitated using the calibration curve generated in this method. However, compounds greater than C_{36} must be reported separately from TPH and must be qualified as estimated. Components lighter than C_9 in products such as gasoline are also detectable but may be completely or partially lost during sample preparation.

1.3 The Reporting limits commonly used are as follows for the applicable matrices (preparative methods are listed in section 2.0):

Matrix	Weight Vol	Final Extract Vol	MRL
Water	1.0 liter	1.0 ml	200 ppb
Soil	20-30 g	1.0 ml	37.5-25 ppm
Waste Oil	1.0 g	10 ml	7500 ppm

2.0 Method Summary

2.1 This TPH method provides gas chromatographic conditions for the detection of total petroleum hydrocarbons in the C_9-C_{36} range. This procedure is based on a solvent extraction followed by analysis on a high-resolution capillary column gas chromatograph with duel flame ionization detectors. Sample preparation is discussed separately in the respective preparation SOP.

2.2 A capillary column and temperature program is used in the gas chromatograph to separate the organic compounds and a Flame Ionization Detector (FID) achieves detection.

2.3 Samples can be prepared by one of the following extraction methods, refer to the appropriate SOP:

Matrix	Method #	Method Summary
Water	3510	Separatory Funnel Liquid-Liquid Extraction
Soil	3541	Automated Soxhlet Extraction
Soil	3546	Microwave Extraction
Soil	3550	Ultrasonic Extraction
Oil	3580	Waste Dilution

3.0 HEALTH AND SAFETY

3.1 Each employee has been trained and has acknowledged being trained in the safe use and handling of chemicals being used in the laboratory. This training has been performed according to the ESS Training SOP 80_0016 and by the Chemical Hygiene Plan SOP 90_0001 in conjunction with the Safety orientation

3.2 To minimize exposure, process samples in an exhaust hood or well-ventilated workspace. When working with samples and chemicals, wear gloves to minimize contact and possible absorption. Always wear appropriate eye protection.

3.3 Proper emergency response to spills or injury should be reviewed by the laboratory employee prior to attempting this procedure. This includes location of spill kits, emergency eyewash and showers, fire fighting equipment, as well as evacuation routes.

3.4 Material Safety Data Sheets are available for all chemicals used in this procedure. All laboratory employees are required to read these before handling these chemicals.

4.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING AND STORAGE

4.1 Aqueous samples are collected in 1 liter amber glass bottles with Teflon-lined screw caps. Aqueous samples are preserved to a pH of <2 with 1:1 HCl and cooled to 4°C immediately after collection.

4.2 Soil and sediment samples are collected in 4 oz (120 ml) wide-mouth glass jars with Teflon-lined screw caps and cooled to 4°C immediately after collection.

4.3 Aqueous samples must be extracted within 7 days of collection, and analyzed within 40 days of extraction.

4.4 Soil and sediment samples must be extracted within 14 days of collection, and analyzed within 40 days of extraction.

5.0 INTERFERENCES AND POTENTIAL PROBLEMS

5.1 Method interferences are reduced by washing all glassware with hot soapy water and then rinsing with warm tap water, acetone or methanol, and methylene chloride.

5.2 High purity reagents must be used to minimize interference problems.

5.3 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. Whenever an unusually concentrated sample is analyzed, it must be followed by the analysis of a system solvent blank to check for cross-contamination.

5.4 To minimize mass discrimination, the injection system must be cleaned on a regular basis. Loss of hydrocarbon C_{28} – C_{36} response can occur after running highly contaminated samples.

5.5 C36 response is greatly affected by the length of column inserted into the injection port. To meet Connecticut criteria insert a column length of 4-5 mm.

6.0 APPARATUS AND MATERIALS

6.1 Gas Chromatograph HP 5890 Series II.

6.2 HP7673 Autosamplers.

6.3 Dual FID (Flame Ionization Detector).

6.4 Column DB-5 (J&W) 30m * 0.25 mm ID * 0.5 um film thickness or equivalent

6.5 Vials.

6.5.1 Sample vials with Teflon lined crimp tops.

6.5.2 14 ml glass vials with Teflon lined caps.

6.6 Volumetric flasks 10 ml-100 ml.

6.7 Microsyringes 10 µl, 100 µl , 250 µl, 500 µl, 1000 µl.

6.8 **Data system**:

6.8.1 **Computer:** The Semi-Volatiles laboratory has one GC/FID system analyzing method 8100-mod. SVOA GC2 has an AST computer with a Windows 95 operating system. All computer systems are networked to a Windows 2003 server, which is the destination of all files. A differential back-up is performed nightly and a full back is performed each weekend using Symantec Backup Exec to tapes. As the systems acquires and stores data onto the server, the server becomes full. The data is downloaded and archived onto an external hard drive.

6.8.2 **Software:** HP/Agilent Environmental Chemstation - The software is interfaced to the flame ionization detectors and allows the continuous acquisition and storage on machine-readable media of all chromatograms obtained throughout the duration of the instrument program. The software is capable of integrating the abundance in any EICP between specified times. Current versions G1045A version 01.00.

7.0 REAGENTS AND STANDARDS

7.1 **Reagents**

7.1.1 Reagent Water: organic free water (ASTM Type I reagent grade water).

7.1.2 Solvents: methylene chloride and acetone methanol; pesticide grade or better. Store away from other solvents.

7.1.3 Sodium sulfate: (ACS) granular, anhydrous.

7.1.4 Ottawa and/or masonry sand: free of extractable petroleum hydrocarbons.

7.2 **Standards**: Store all standard solutions (primary, stock, working, and surrogate) at room temperature in the dark.

7.2.1 **Primary Standards**: Unopened primary standards are not kept beyond the manufacturer's expiration date and, once opened, primary standards are not kept beyond six months, or the manufacturer's expiration date (whichever comes first).

Solution name	Concentration	Vendor	Cat #
Aliphatic Hydrocarbon Standard	1000 µg/ml	Ultra	SMA-310
Aliphatic Hydrocarbon Standard (Second source)	1000 µg/ml	Accustandard	*
o-Terphenyl	2000 µg/ml	Ultra	IST-480

* Proposed Mass DEP – Aliphatic Hydrocarbons DRH-007S

All solutions are stored at room temperature.

7.2.2 **Calibration Stock Standard:** This calibration standard is prepared by making a 1:2 dilution of the primary standard. Five ml of the primary aliphatic hydrocarbon standard and 2.5 ml of the o-Terphenyl primary standard is diluted to 10 ml in a 10 ml class A volumetric with methylene chloride. The final concentration for these standards will be 500 mg/L. The following analytes are in this mix:

Carbon #		Carbon #		Carbon #	
9	n-Nonane	**18**	n- Octodecane	**26**	n- Hexacosane
10	n-Decane	**19**	n-Nonadecane	**28**	n-Octacosane
12	n- Dodecane	**20**	n-Eicosane	**30**	n- Triacontane
14	n-Tetradecane	**22**	n- Docosane	**36**	n-Hexatriacontane
16	n- Hexadecane	**24**	n- Tetracosane		

o-Terphenyl

7.2.3 **Working Calibration Standards**

7.2.3.1 The lower linear range of the system is defined as the collective response of the 14 aliphatic compounds (70-ppm). The upper linear range for the collective C_9-C_{36} aliphatics is defined by peak height measurement based upon the maximum peak height documented for

the 500-ppm aliphatic working standard. If the 500 µg/ml standard is not used for calibration then the 250 µg/ml standard will define the linear dynamic range

7.2.3.2 Prepare working solutions for initial and daily calibrations by transferring the following volumes of stock solution using Methylene Chloride as a solvent.

Cal Stock Conc.	Vol. added	Final Vol.	Final Aliph.Conc.	C_9-C_{36} Conc.
500 ug/ml	1000 ul	1.0 ml	500 ug/ml	7000
500 ug/ml	500 ul	1.0 ml	250 ug/ml	3500
500 ug/ml	200 ul	1.0 ml	100 ug/ml (CCV)	1400
500 ug/ml	100 ul	1.0 ml	50 ug/ml	700
500 ug/ml	20 ul	1.0 ml	10 ug/ml	140
500 ug/ml	10 ul	1.0 ml	5 ug/ml	70
10 ug/ml	100 ul	1.0 ml	1 ug/ml	14

7.2.4 **Second Source calibration standards-** A calibration stock standard (500 ug/ml) and working initial calibration verification standard (100 ug/ml) are prepared in the same manner as the calibration standards.

8.0 PROCEDURE

8.1 Instrument Set-Up

8.1.1 All daily maintenance, as recommended by the instrument manufacturer, must be performed on the GC before analysis can be run. This must be recorded in the maintenance Logbook. See section 18.0 for maintenance and troubleshooting.

8.1.2 The chromatographic conditions have been optimized using a high resolution capillary column with a slow ramp rate from 50°C to 310°C. The total run time is over 25 minutes. The resulting chromatogram provides extensive chromatographic information covering a wide range of materials including, but not limited to, light and medium fuel oils, heavy oils (such as crude oils), coal tar, and lubricating oils.

8.1.3 The column must resolve diesel components and the solvent front from C_9.

8.1.4 Settings

	Injectors A and B
Injection port temperature	290°C
Detector temperature	300°C
Injection volume	1- 2 ul
Recommended carrier gas H2 :	0.5 to 1.5 ml/min
Air:	400 ml/min

Hydrogen: 35 ml/min

8.2 Instrument Calibration

8.2.1 ESS Laboratory's policy is that the audit trail on the Chemstation/Enviroquant software is always on. This ensures that any changes made to the instrument operating method be documented through the audit trail.

8.2.2 Calibrate the GC with five to seven calibration working standards. The GC System is calibrated using the external standard method.

8.2.3 Prepare Aliphatic Hydrocarbon calibration standards at a minimum of five concentration levels, see 7.2.3.2.

8.2.4 Inject each calibration standard using the technique that will be used to introduce the actual samples into the gas chromatograph (e.g., 2 µl injections).

8.2.5 Tabulate the area responses against the mass of TPH injected. This applies to the individual aliphatic compounds as well as the C_9-C_{36} range. The C_9-C_{36} retention time (Rt) window is defined as the Rt of n-Nonane (C_9) to the Rt of n-Hexatriacontane (C_{36}). The results are used to prepare a calibration curve for the individual aliphatic compounds, as well as the TPH range. The ratio of the response to the amount injected, defined as the calibration factor (CF), is calculated at each standard concentration using Equation 1. This is accomplished through the EnviroQuant software. ***After generating the initial calibration curve in Enviroquant, the analyst must visually check that each calibration standard was entered into the new calibration method. This is accomplished by checking that the area response for one compound or range from each calibration standard's printout corresponds to the area count listed in the calibration method in Enviroquant.***

Equation 1

$$\textbf{Calibration Factor (CF)} = \frac{(A_S)}{(C_S)}$$

Where:

A_S = Area for TPH in the standard (C_9-C_{36} range or individual aliphatic compounds).

C_S = Mass of TPH injected, ng.

8.2.5.1 If the percent relative standard deviation (%RSD) of the calibration factors is equal to or less than 20% for the calibration standards, as determined using Equation 2, linearity through the origin can be assumed. Refer to Tables 1 & 2 in Section 10.4.

8.2.5.2 If the system does not meet this standard, then a linear regression calibration curve may be used. If linear regression is used, then at a minimum, the correlation coefficient, r, must be $\geq$ 0.99.

8.2.5.3 Any individual standard can be omitted. A minimum of five points are needed to satisfy method requirements. Omission of a point will redefine the calibration range. Dilutions will be made accordingly.

8.2.5.4 If the system does not meet these standards then the calibration data is not acceptable. If the calibration does not pass the system may need to be maintained and a new calibration performed.

Equation 2: **Percent Relative Standard Deviation**

$$\% \text{ RSD} = \frac{\text{Stand Dev of 5 CFs} \times 100\%}{\text{Mean of 5 CFs}}$$

8.2.6 **Initial Calibration verification standard (ICV) –** Immediately following generation of an initial calibration a second source standard mid level calibration is run after each initial calibration. The concentration of the individual aliphatic compounds as well as the TPH C_9-C_{36} range in the second source must be within 20 %Difference/Drift of the expected value. Percent Drift is used when linear regression is used for the initial calibration. %Drift is calculated as %recovery of ICV value versus actual concentration. See Section 10 for method-specific exceptions. Percent Difference is calculated as follows:

Equation 3:

$$\textbf{Percent Difference } (\%D) = \frac{R_2 - R_1}{R_1} \times 100\%$$

Where:

$R_1 = \overline{CF}$ from the calibration (average calibration factor)
R_2 = CF from the check standard

8.2.7 **Continuing Calibration Verification:** At a minimum, the CF of the $C_9 - C_{36}$ TPH range and individual aliphatic compounds must be verified on each working day prior to sample analysis. It must also be verified after every 20 samples (10 field samples for DoD/Navy/AFCEE) or 12 hours. This is performed by the injection of a mid-level calibration standard to verify instrument performance and linearity. If the percent difference/drift (%D) for the TPH range and individual aliphatic compounds varies from the predicted response by more than ±20%, as calculated using Equation 3. See corrective action in Section 10.0 for CCVs that are outside criterion. **(The CCV concentration, when performing DoD/Navy work must be at a minimum two different concentrations throughout the analytical run. One standard must be at or below the mid-range standard.)** ESS Lab

alternates between the 50 ppm and 100 ppm standards. Refer to Tables 1 & 2 in Section 10.4.

8.2.8 Record continuing calibration acceptability, if applicable, on attachment A.

8.3 SAMPLE ANALYSIS

8.3.1 Prior to running samples, a midlevel calibration standard must be analyzed to verify the curve (8.2.6). This calibration standard is analyzed under the same conditions as the calibration curve. Once the instrument has a valid continuing calibration, sample analysis may begin.

8.3.2 State of Connecticut ETPH Mass Discrimination protocol requires that the first CCAL standard in a sequence be evaluated for mass discrimination. The response factor from each alkane (C_9-C_{36}) is compared to the average response factor of all the alkanes in the initial calibration. An individual alkane response factor cannot drift more than 20% from the average; one exceedance is allowed but must be less than 50 %. Any other deviations must be described in the project narrative. The injector system must be kept very clean to meet these criteria. This requirement is applicable only to Connecticut samples.

8.3.3 Mass DEP also requires a mass discrimination check. The ratio of C_{28}/C_{20} must be > 0.85.

8.3.4 **Log Book**: All samples set up on the instrument must be entered into the run logbook (Attachment B) prior to sample analysis. The logbook must be filled out completely with the date, vial number (slot number), computer file number, method number, ESS lab ID, and the initials of the analyst setting up the instrument.

8.3.4.1 Date includes the day, month, and year.

8.3.4.2 Vial number: This field ***must*** be filled in for each entry.

8.3.4.3 Computer file ID is an instrument abbreviation, using a perpetual numbering system beginning at the start of a new year with e.g.G2F0001 and going to the end of the year.

8.3.4.4 The ESS Lab ID includes the ID of the standards, samples and all QC samples.

8.3.4.5 Initials are signed by the analyst setting up the instrument.

8.3.4.6 The Comment section is a summary of calibration results, dilution information, and any unusual observations. (Examples would include: carry over information into the sample, retention time shift, calibration standard is less than 20% recovery, sample needs dilution.)

8.3.4.7 The Method section is the method in the chromatographic software used to operate the instrument.

8.3.5 Quality control samples are to be analyzed with their associated batches. It is not acceptable to batch QC samples together. The following is the recommended analytical sequence for an analytical batch.

8.3.5.1 Preparation Blank

8.3.5.2 Blank spike /blank spike duplicate

8.3.5.3 Environmental samples 1 to 20

8.3.5.4 Continuing Calibration verification standard (CCV)

8.3.6 A CCV is analyzed at the beginning, after every 20 samples and/or at the end of the analytical sequence. Also, the CCV must be analyzed every 12 hours. **Note: When analyzing samples for DoD/Navy/AFCEE work CCVs must be analyzed after every 10 field samples.** The final CCV must be at a different concentration than the initial CCV; alternate between 100 and 50 ppm.

8.3.7 Quantitative analysis of the Total petroleum hydrocarbons in the sample is accomplished by comparing the total area between the retention time of n-C_9 and n-C_{36}. The absolute retention times used to measure this range are determined from the continuing calibration standard analyzed just prior to the samples. This range is integrated with a forced baseline using the GC EnviroQuant Software.

8.3.8 The surrogate peak is also integrated.

8.4 Retention Time Windows:

8.4.1 Total Petroleum Hydrocarbon Ranges: TPH retention time (Rt) windows are defined before the Rt of the beginning marker compound (C_9) and after the Rt of the ending marker compound (C_{36}). The retention time windows are set daily by the Rt of the beginning and ending markers in the initial continuing calibration verification standard (CCV).

9.0 CALCULATIONS

9.1 Calculation – Waters

$$mg/L = \frac{(A)(DF)(Vt)}{(CF_{avg})(Vi)(V)}$$

9.2 Calculation - Soils

$$\text{mg/Kg dry wt.} = \frac{(A)(DF)(Vt)}{(CF_{avg})(Vi)(Wt)(\%\ Solid)}$$

Where:

A = (Total Area)-(Area of Surrogate)
DF = Dilution Factor
Vt = Final Volume of Extract (ul)
Vi = Volume injected (ul)
CF_{avg} = Average of Range Calibration Factor (from Initial Calibration)
V = Volume of sample (ml)
Wt = Wet Weight of Sample
% Solid = % Solid expressed as a decimal

10.0 Quality Assurance/Quality Control Requirements

10.1 Immediately after the initial calibration, a second source standard (ICV) is analyzed. This standard is prepared at the Level 3 concentration. The percent recovery of the second source must be ±20%. If the percent recovery is outside criterion, then corrective action must be taken. Perform instrument maintenance and/or prepare a new second source standard. If the second analysis of the ICV is not within criterion, then a new calibration curve must be generated. ***Sample analysis cannot begin until a valid second source has been analyzed.***

10.2 Accuracy and Precision**:** All laboratory personnel must demonstrate initial proficiency for each sample preparation method/matrix that he or she performs. All new employees must successfully demonstrate initial proficiency prior to independently performing analysis on real samples. This must be accomplished by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The initial proficiency results will become part of each employee's training file.

QC Sample Preparation:

Spiking Solution: Four QC samples must be prepared from a spiking solution with the analytes of interest. The spiking solution must be made using standards **prepared independently from those used for calibration**. The QC samples must be prepared at a concentration that would result in data falling within the middle of the calibration curve. In most cases the blank spike or matrix spike solution is used. Prep: The samples are prepared in a clean matrix. In most cases this initial demonstration will simply be a matter of preparing four blank spikes with a batch of samples.

QC Sample Analysis: The four QC samples must be analyzed within the criteria of the method being evaluated. The QC samples must be handled in exactly the same manner as actual samples.

Accuracy Calculation: Accuracy is defined as the closeness of agreement between an observed value and an accepted reference value. Each of the four spiked samples will be calculated for percent recovery. The average of the percent recovery values is the accuracy result.

Precision Calculation: Precision is defined as the agreement of a set of replicate measurements without assumption of knowledge of the true value. Precision is estimated by the relative standard deviation (RSD) of the four QC samples.

%RSD = (s / x) 100 %

Where:
s = Standard Deviation of a finite number of values. On a scientific calculator use the **σxn-1** key.

$\bar{x}$ = The average of the four QC sample % recoveries.

Reporting Accuracy and Precision**: Report Accuracy and Precision data with the following minimum info:**

Matrix: Prep Method:
Clean-up Method: Analysis Method:
Date Extracted: Date Analyzed:
Sample Prepared by: If Applicable Sample Analyzed by:

Parameter	*% Rec. QC 1*	*% Rec. QC 2*	*% Rec. QC 3*	*% Rec. QC 4*	*Average Recovery*	*Standard Deviation*	*%RSD*

10.2.1 **Interpretation of Results**: The percent recoveries should be between 50-130% and the %RSD should be less than 30%. If any of the accuracy and precision results do not fall within the criteria then re-prep and re-analyze all QC samples only for those analytes that were not within criteria.

10.3 Each day the analysis is performed the initial calibration must be verified. See Tables 1 and 2. Continuing calibration verification (CCV) must be performed at the beginning and end of each analytical sequence; see 8.2.7 for frequency of CCV. The response factors for the calibration should be within 20 percent of the initial calibration. **(The CCV concentration, when performing DoD/Navy work must be at different concentrations throughout the analytical run. One standard must be at or below the mid-range standard..)** When a CCV is out of this acceptance window, the laboratory should stop analyses and take the following corrective action:

10.3.1 If criterion is exceeded then remake and re-analyze CCV. If second consecutive CCV is within criteria then calibration is verified, otherwise re-calibrate system and re-analyze any sample analyzed after invalid CCV.

10.3.2 If the second consecutive CCV was outside criterion, then the analyst may choose to demonstrate acceptability of initial calibration by the analysis of two consecutive CCVs at two concentrations. ***Exception: If CCV is exhibiting high bias (concentration is higher than upper limit) then any samples that are non-detect for that analyte may be reported.***

10.3.3 If the above corrective action fails, then a new five point initial calibration must be generated.

10.3.4 When performing analysis for MA MCP, Navy, USACE, DoD, or AFCEE any analyte/range outside of criteria in the CCV must be noted in the project narrative

10.4 From the beginning CCV, the retention time of the surrogate and the C_9-C_{36} range markers are determined.

Table 1

TPH (C9-C36) Criteria:						
ICAL:						
Mth	**Stds**	**C9-C36 Rng %RSD / Linearity**	**Aliphatic Cmpd %RSD / Linearity**	**ICV**	**Mass Discrim.**	**RT Window**
CT ETPH	Min of 5pts	30% / 0.99	30%/0.99	30%D	After Ical RF<20% w/ 1 <50%	Ical Avg Rt
MA TPH	Min of 5pts	25%/0.99	25%/0.99	20%D	C28/C20 >0.85	Ical Avg Rt
DOD	Min of 5pts	20%/0.995	20%/0.995	20%D	Refer to State	Ical Avg Rt
8100M	Min of 5pts	20%/0.99	20%/0.99	20%D	NA	Ical Avg Rt
CCAL:						
Mth	**Stds**	**Mass Discrim.**	**C9-C36 Rng CCV**	**Aliphatic Analyte CCV**	**RT Window**	
CT ETPH	Mid Pt	Beginning 12hr Seq RF<20% w/ 1 <50%	30%D End CCV recommended Every 12 hrs or 20 smp.	30%D End CCV recommended Every 12 hrs or 20 smp.	Update from beginning CCV	
MA TPH	Mid Pt	Beginning 12hr Seq C28/C20 > 0.85	25%D End CCV no failures Every 12 hrs or 20 smp.	25%D End CCV 4 failures <40% Every 12 hrs or 20 smp.	Update from beginning CCV	

DOD	Alternate Concentration	Refer to State	20%D End CCV no failures Every 10 smp.	20%D End CCV no failures Every 10 smp.	Update from beginning CCV	
8100M	Mid Pt	NA	20%D End CCV no failures Every 12 hrs or 20 smp.	20%D End CCV 4 failures <40% Every 12 hrs or 20 smp.	Update from beginning CCV	

Table 2

DRO (C10-C28) Criteria:						
ICAL:						
Mth	**Stds**	**C10-C28 Rng %RSD / Linearity**	**Aliphatic Cmpd %RSD/Linearity**	**ICV**	**Resolution**	**RT Window**
8015	Min of 5pts	20%/0.99	20%/0.99	20%D	NA	Ical Avg Rt
ME DRO	Min of 3pts	20%/0.99	20%/0.99	20%D	C17/C18 > 60%	Ical Avg Rt
DOD	Min of 5pts	20%/0.995	20%/0.995	20%D	NA	Ical Avg Rt
CCAL:						
Mth	**Stds**	**Resolution**	**C10-C28 Rng CCV**	**Aliphatic Analyte CCV**	**RT Window**	
8015	Mid Pt	NA	20%D failures End CCV no Every 12 hrs or 20 smp.	20%D End CCV no failures Every 12 hrs or 20 smp.	Update from beginning CCV	
ME DRO	Seq Begin w/ Mid Pt & Res Std End With Mid Pt & LL Commercial Diesel	At end of Seq: C17/C18 > 60%	20%D failures End CCV no Every 20 smp.	20%D End CCV no failures Every 20 smp.	Update from beginning CCV	
DOD	Alternate Mid and Low See State Mth	NA	20%D failures End CCV no Every 10 smp.	20%D End CCV no failures Every 10 smp.	Update from beginning CCV	

10.5 Preparation Blanks

10.5.1 Preparation blanks are used to verify the presence or absence of method contamination. They are prepared from controlled matrices in the same manner to that of the environmental samples.

10.5.2 Preparation blanks should follow the associated environmental samples through all phases of the sample preparation and in the analytical process.

10.5.3 For a preparation blank to be considered valid it must meet the same instrumental criteria as any other sample and the surrogate recovery of the preparation blank must meet the normal recovery criteria.

10.5.4 The preparation blank should not contain any material at a level above ½ the MRL. See section 11.0 for corrective action

10.6 **Blank Spike/Blank Spike Duplicate Samples**

10.6.1 Blank Spike/Blank Spike Duplicate Samples (BS/BSD) are prepared from a second source standard of aliphatic hydrocarbons. A 50 ppm standard is made by diluting 5 ml of the 1000 ppm standard (supplied by accustandard) to 100ml in methylene chloride. 1.0 ml of this 50 ppm solution is then spiked into a clean matrix to prepare the BS/BSD.

10.6.2 The BS/BSD must follow the associated environmental sample through all phases of the sample preparation and analysis process.

10.6.3 The BS/BSD should not contain any other material except for the spiked material at a level above the reporting limit. The BS should meet the spike recovery criteria of 40% - 140% and the % RPD between the BS and BSD must be less than 25%. In the case of the State of Connecticut, ETPH QC criteria are 60-120% for Recovery and ≤ 30% for RPD.

10.6.4 Surrogate QC recovery criteria are 40-140%, except for State of Connecticut which are 50-150 %.

10.6.5 . See Section 11.0 for corrective action.

10.7 **Matrix Spikes/Matrix Spike duplicate**

10.7.1 MS/MSDs are performed on each matrix where sample is available. The same spike is used as in 10.6.1.

10.7.2 The MS should meet the spike recovery criteria of 40% - 140% and the MS/MSD should have a %RPD of +/- 50%. In the case of the State of Connecticut, ETPH QC criteria are 50-150% for Recovery and ≤ 30% for RPD.

10.7.3 If the MS/MSD is outside of the acceptance criteria then it must be determined if it is a Matrix Effect or Laboratory error. See Section 11.0 for corrective action.

10.8 **Method Detection Limit Study: MDLs** are determined in either reagent water or sodium sulfate and verified annually. MDLs are calculated, reported and verified according to the ESS SOP 110_0013. (Project-specific requirements may require that the MDL study be performed in the site-specific matrix.). Seven MDL samples are extracted and analyzed like any other sample in an analytical batch that contains a method blank. The MDL samples are prepared as follows:

10.8.1 **Soil MDL**: 250 ul of a 2000ug/ml Fuel Oil # 2 solution (1:10 dilution of spiking solution in 10.6.1) is added to 30g (20g for method 3541) of sodium sulfate.

10.8.2 **Aqueous MDL**: 200 ul of a 2000ug/ml Fuel Oil # 2 (1:10 dilution of spiking solution in 10.6.1) solution is added to 1 Liter of Lab DI water.

10.9 **Control charts** are generated in accordance with SOP 110.0014.

11.0 DATA VALIDATION

11.1 Data validation will be accomplished by reviewing all of the quality control parameters and assuring that they are within recommended ranges by completing the Data Review Checklist for GC/FID 8100M. The only exceptions made to ranges would be the following:

11.1.1 For MS/MSD, the RPD should be +/- 50% (≤ 30% for CT). However, there are cases where duplicates may not work. If this is the case, inform client in narrative concerning sample non-homogeneity.

11.1.2 For matrix spikes, the % Recovery should be 40-140% (50-150 % for CT). If the matrix spike is outside this range, check the BS/BSD. If the BS/BSD is within limits, matrix interferences are present and should be noted in the narrative.

11.1.3 Analytical batches with Method blanks above the ½ MRL will be re-prepped and re-analyzed with the following exceptions:

11.1.3.1 Samples that are that are at least twenty times higher than the method blank may be reported.

11.1.3.2 When the method blank is less than 5% of the regulatory limit associated with the analyte the method blank would be acceptable.

11.1.3.3 If the analyte is found in the method blank above the ½ the MRL but is not in any of the associated samples, no corrective action is needed.

11.1.3.4 Any results that are reported with method blank contamination must be B-flagged.

11.1.4 For the BS/BSD, the % Recovery should be 40-140% (60-120 % for CT). If the BS/BSD is outside this criterion, the analytical batch will be re-extracted and re-analyzed with the following exceptions:

11.1.4.1 For BS/BSD >140% (>120% for CT) , samples with results below the MRL may be reported. It has been shown that the results above MRL would have been detected.

11.1.4.2 For BS/BSD < 40% (< 60% for CT) , samples with results above a regulatory limit may be reported.

11.1.4.3 In some instances there may be insufficient sample to re-extract. The results may be reported as estimated values when this occurs after contacting the client for instructions.

11.1.4.4 Any samples that are reported with invalid BS/BSD data must have a notation in the case narrative.

11.2 All unusual observations and method deviations will be noted in the narrative accompanying the data report presented to the client.

11.3 A second analyst reviews all data for accuracy. Results of this review are noted on the data validation checklist in the second level review column and in the comment section.

12.0 REFERENCES

12.1 SW846 Method 8015B, Nonhalogenated Organics Using GC/FID Third Edition, Update III.

12.2 SW846 Method 8100, Polynuclear Aromatic Hydrocarbons, Third Edition, Update III.

12.3 Univ. Connecticut, Analysis of Extractable Total petroleum hydrocarbons (ETPH) Using Gas Chromatograph/Flame Ionization Detection, March 1999.

12.4 NELAC Standards, Chapter 5, June 2003.

12.5 DoD QSM Final Version 4.1, April 2009.

13.0 POLLUTION PREVENTION and WASTE MANAGEMENT

13.1 ESS Laboratory's policies on pollution prevention and waste management are covered in SOP 90_0002, Hazardous Waste Contingency and Emergency Response Plan. All employees are trained in the requirements of the SOP.

14.0 METHOD PERFORMANCE

14.1 Precision and Accuracy data must be generated by all employees before performing this analysis on client samples. The data is generated by analyzing a method blank and four blank spike samples. Acceptance criteria are 40-140% Recovery and %RSD of ≤ 25%.

14.2 The precision and accuracy data in Table 1 were developed using this method.

15.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

Table 1. Typical Precision and Accuracy data generated 4/23/05 – 2/14/07

Compound	Prep Method	Spk	Avg	%Rec	%RSD
Total Petroleum Hydrocarbons	3510C	20	13.38	66.9	7.87
Total Petroleum Hydrocarbons	3541	20	11.38	56.9	7.03
Total Petroleum Hydrocarbons	3550B	20	14.3	71.5	6.71

16.0 DEFINITIONS

16.1 **Accuracy**: The closeness of agreement between an observed value and an accepted reference value. When applied to a set of observed values, accuracy will be a combination of a random component and of a common systematic error (or bias) component.

16.2 **Batch**: A group of samples which behave similarly with respect to the sampling or the testing procedures being employed and which are processed as a unit. For QC purposes, if the number of samples in a group is greater than 20, then each group of 20 samples or less will all be handled as a separate batch.

16.3 **Bias**: The deviation due to matrix effects of the measured value (x_s - x_u) from a known spiked amount, where x_s is the spiked sample and x_u is the un-spiked sample. Bias can be assessed by comparing a measured value to an accepted reference value in a sample of known concentration or by determining the recovery of a known amount of contaminant spiked into a sample (matrix spike).

16.4 **Control Sample**: A QC sample introduced into a process to monitor the performance of the system.

16.5 **Equipment Blank**: A sample of analyte-free media which has been used to rinse the sampling equipment. It is collected after completion of decontamination and prior to sampling. This blank is useful in documenting adequate decontamination of sampling equipment.

16.6 **Method Reporting Limit**: The lowest concentration that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions. The MRL is generally 5 to 10 times the MDL. ESS Laboratory sets the MRL to the lowest non-zero standard in the calibration curve or higher.

16.7 **Field Duplicates**: Independent samples which are collected as close as possible to the same point in space and time. They are two separate samples taken from the same source, stored in separate containers, and analyzed independently. These duplicates are useful in documenting the precision of the sampling process.

16.8 **Blank Spike (BS)**: A known matrix spiked with compound(s) representative of the target analytes. This is used to document laboratory performance.

16.9 **Matrix**: The component or substrate (e.g., surface water, drinking water) which contains the analyte of interest.

16.10 **Matrix Duplicate**: An intra-laboratory split sample which is used to document the precision of a method in a given sample matrix.

16.11 **Matrix Spike**: An aliquot of sample spiked with a known concentration of target analyte(s). The spiking occurs prior to sample preparation and analysis. A matrix spike is used to document the bias of a method in a given sample matrix.

16.12 **Matrix Spike Duplicates**: Intra-laboratory split samples spiked with identical concentrations of target analyte(s). The spiking occurs prior to sample preparation and analysis. They are used to document the precision and bias of a method in a given sample matrix.

16.13 **Method Blank**: An analyte-free matrix to which all reagents are added in the same volumes or proportions as used in sample processing. The method blank should be carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.

16.14 **Method Detection Limit (MDL)**: The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix type containing the analyte. See SOP 110_0013 for further explanation.

16.15 **Records**: Include all logbooks, papers, machine readable materials, or other documentary materials, regardless of physical form or characteristics.

16.16 **Surrogate**: An organic compound which is similar to the target analyte(s) in chemical composition and behavior in the analytical process, but which is not normally found in environmental samples.

17.0 PERSONNEL QUALIFICATIONS

17.1 Analysts who perform this analysis must have a working knowledge or quantitative and qualitative analysis, instrumental methods of analysis, chemical laboratory methods, and equipment.

17.2 All analysts, before performing any analysis, participate in the ESS Laboratory training program (SOP80_0016). The training process consists of reading the Standard Operating Procedure, gaining instruction on the procedure from an experienced analyst, and performing the initial demonstration of capability.

18.0 TROUBLESHOOTING

18.1 The following procedure is performed when the instrument is initially set up or when a continuing calibration has failed the QC criteria.

18.1.1 Set the GC system to room temperature and turn off oven.

18.1.2 Remove column by unscrewing the column in the injection port.

18.1.3 Remove septum nut and septa. Discard septa.

18.1.4 Remove weldment. This will expose the O-ring and glass liner. Using a set of tweezers, remove O-ring and liner. If O-ring is not distorted then set aside for later use, otherwise, replace O-ring. Remove the glass liner. In a ventilation hood rinse the liner with methylene chloride and scrub with a cotton swab. If the liner is visibly stained, then replace with a new one.

18.1.5 With a cotton swab dipped in methanol, clean the injection port and weldment.

18.1.6 Remove the gold seal nut located on the bottom of the injection port. With a cotton swab and methanol, clean the gold seal.

18.1.7 Replace all parts in the following order:

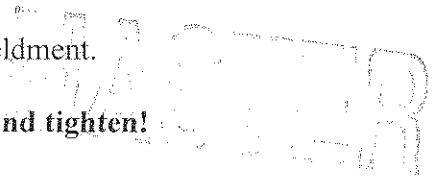
18.1.7.1 Gold seal nut. Hand tighten and ¼ turn with wrench.

18.1.7.2 Insert clean or new glass liner.

18.1.7.3 Place O-ring over liner. Slide O-ring over and down the liner until it fits snug against the injection port.

18.1.7.4 Replace weldment.

18.1.7.5 Place new green septa into weldment.



18.1.7.6 Replace septum nut. **Only hand tighten!**

18.1.7.7 Slide column nut and a new graphite ferrule over column.

18.1.7.8 Using a ceramic tile, cut 3-6 inches of the column. The cut must be square with no jagged edges.

18.1.7.9 Connect column to injection port by inserting 3 mm of column into the injection port and hand tighten column nut. Next add ¼ turn with a wrench.

18.1.8 Make sure all gases are flowing. (Measure flows with bubble meter.) The flow should be approximately 1 ml/min going through a capillary column (0.25 um ID).

18.1.9 Turn on injection port temperature.

18.1.10 Set oven temperature to 150°C and allow the system to stabilize. Bake out the oven at 300°C for an hour. Reset to 80°C.

18.2 Record all maintenance in the instrument's maintenance logbook.

19.0 Data Management And Records

19.1 **Data Management** - ESS Laboratory's utilizes the Promium Element LIMS system as part of its Data Management system. Client sample information is entered into ELEMENT LIMS and analyses are assigned to each sample. The LIMS allows EPA hold times, minimum batch QC requirements, and QC criteria to be assigned to each analysis. Standards can be entered and assigned to QC samples through the LIMS. Once analysis has been performed, data is imported using DataTool avoiding manual errors. In conjunction with Crystal Reports, the ELEMENT system allows for a wide variety of reporting formats.

19.2 **Records** – The specific retention periods required in the NELAC Standards, EPA-CFR and state and local statutes are followed or exceeded. At a minimum, data records are retained for five years from last use (10 years for drinking water). If there is a question about whether a record should be retained or disposed because no specific requirement could be found, the record is retained until such time as a retention period is specified. Records are stored in specified-labeled locations and are easily retrievable. All raw data associated with testing is also retained including; computer printouts, chromatograms, review forms, and logbooks.

ATTACHMENTS

Attachment A – GC2 Rear Sequence Log

Attachment B – GC2 Front Sequence Log

Attachment C– Instrument Control Parameters

Attachment A

Data Reporting **Instrument:** _____ **Matrix:** _____

ESS Laboratory (SVOA)
GC2 Rear Sequence Log

Work Orders Reported: _____

Date Analyzed: _____ Analyst: _____

	Method	Seq ID	Calibration ID
Soil			
Aqueous			

Vial	File	Lab Id	Rw	Rpt	Imp	STD ID/ Comments	Batch ID	Matrix	-RE

ICAL/CCAL Failures: _____

Comments: _____

ICAL Batch ID: BB71630(Aq); BB71631(Soil)

Final Data Review: _____

Signed copy included with each work c

Control #60.0046-0801A

Lobgook Review: _____

Attachment B

ESS Laboratory (SVOA)
GC2 Rear Sequence Log

Work Orders Reported: _____

Date Analyzed: _____ Analyst: _____

	Method	Seq ID	Calibration ID
Soil			
Aqueous			

Vial	File	Lab Id	Rw	Rpt	Imp	STD ID/ Comments	Batch ID	Matrix

ICAL/CCAL Failures: _____

Comments: _____

ICAL Batch ID: BB71630(Aq); BB71631(Soil)

Final Data Review: _____
Signed copy included with each v

Control #60.0046-0801A

Lobgook Review: _____

Attachment C

TOPLEVEL PARAMETERS

Method Information For: C:\HPCHEM\1\METHODS\8100SIG1.M

8100m method as of 5.15.01

Method Sections To Run:

( ) Save Copy of Method With Data
( ) Pre-Run Cmd/Macro =
(X) Data Acquisition
(X) Data Analysis
( ) Post-Run Cmd/Macro =

Method Comments:
8100m

END OF TOPLEVEL PARAMETERS

INSTRUMENT CONTROL PARAMETERS

Sample Inlet: GC
Injection Source: GC ALS

HP GC Injector

Front Injector:

Sample Washes	2
Sample Pumps	2
Injection Volume	1.0 microliters
Syringe Size	10.0 microliters
On Column	Off
Nanoliter Adapter	Off
PostInj Solvent A Washes	2
PostInj Solvent B Washes	2
Viscosity Delay	2 seconds
Plunger Speed	Fast

Back Injector:
No parameters specified

HP5890 Temperature Parameters

Zone Temperatures:	State	Setpoint
Inlet A:	On	300 C
Inlet B:	On	300 C
Detector A:	On	315 C
Detector B:	On	315 C

Auxiliary: Off 50 C

Oven Parameters:
Oven Equib Time: 0.20 minutes
Oven Max: 320 C
Oven State: On
Cryo State: Off
Cryo Blast: Off
Ambient: 25 C

Oven Program:
Initial Temperature: 80 C
Initial Time: 2.00 minutes

Level	Rate (C/minute)	Final Temperature (C)	Final Time (minutes)
1	20.0	265	0.00
2(A)	30.0	320	12.00
3(B)	0.0	0	0.00

Next Run Time: 25.08 minutes

HP5890 Purge Valve Settings

Inlet Purge	Init Value	On Time	Off Time	Splitless Injection
A	On	0.75	0.00	Yes
B	On	0.75	0.00	Yes

HP5890 Valve and Relay Information

Initial Setpoints:
5890 Valves:
Valve 1: Off Valve 2: Off Valve 3: On Valve 4: On
19405 Valves:
Valve 5: Off Valve 6: Off Valve 7: Off Valve 8: Off
19405 Relays:
Relay 1: Off Relay 2: Off Relay 3: Off Relay 4: Off

HP5890 Detector Information

Detector	Type	State
A	FID	On
B	FID	On

HP5890 Signal Information

Save data for signal 1 only.

Signal	Source	Peak Width	Data Rate	Start Data	Stop Data
	Det A	0.053	5.000	2.20	27.00
	Det B	0.053	5.000	2.50	20.00

END OF INSTRUMENT CONTROL PARAMETERS

DATA ANALYSIS PARAMETERS

Method Name: C:\HPCHEM\1\METHODS\8100SIG1.M

Percent Report Settings

Sort By: Signal

Output Destination
    Screen: No
    Printer: Yes
    File: No

Integration Events: AutoIntegrate

Ge ate Report During Run Method: No

Signal Correlation Window: 0.020

Qualitative Report Settings

Peak Location of Unknown: Apex

Library to Search	Minimum Quality
DEMO.L	0

Integration Events: AutoIntegrate

Report Type: Summary

Output Destination
    Screen: No
    Printer: Yes
    File: No

Generate Report During Run Method: No

Quantitative Report Settings

Report Type: Summary

Output Destination
Screen: No
Printer: Yes
File: No

Generate Report During Run Method: Yes

Alkanes-front-GC4
Calibration Last Updated: Wed May 09 10:39:32 2001

Reference Window: 10.00 Percent
Non-Reference Window: 5.00 Percent
Correlation Window: 0.02 minutes
Default Multiplier: 1.00
Default Sample Concentration: 0.00

Compound Information

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1) O-Terphenyl ( )

Ret. Time 11.28 min., Extract & Integrate from 11.18 to 11.38 min.

Signal		Rel Resp.	Pct. Unc.(rel)	Integration
Tgt	TIC			*** AUTO ***

Lvl	ID	Conc (ppm)	Response
cc		50.000	740010
50		50.000	740010
10		10.000	140447
20		20.000	304691
100		100.000	1495970
250		250.000	4550776
500		500.000	8920253

Qualifier Peak Analysis OFF
Curve Fit: Avg. RF

---

2) C9-C36 ( )

Ret. Time 12.95 min., Extract & Integrate from 3.20 to 22.70 min.

Signal		Rel Resp.	Pct. Unc.(rel)	Integration
Tgt	TIC			*** AUTO ***

Lvl	ID	Conc ( )	Response
cc		700.000	14024122
50		700.000	14024122
10		140.000	2790277
20		280.000	4246069

100	1400.000	21737876
250	3500.000	58809718
500	7000.000	111385989

Qualifier Peak Analysis ON
Curve Fit: Avg. RF

END OF DATA ANALYSIS PARAMETERS
