# Total Petroleum and Saturated Hydrocarbons by Gas Chromatography/Flame Ionization Detector

References: USEPA, Method **8015D** – "Nonhalogenated Organics Using GC/FID", in Test Methods for Evaluating Solid Waste, SW-846, Revision 4, June 2003.

## 1. Scope and Application

**Matrices:** This standard operating procedure (SOP) describes a method for quantification and qualitative fingerprinting of petroleum products in extracts of water, soil, sediment and petroleum products. Extractable petroleum hydrocarbon in petroleum products such as kerosene, aviation fuels, diesel and heating oils may be analyzed by this method, but products with primarily volatile constituents such as gasoline range organic compounds are not amenable to this method. To determine volatile organic material, see Alpha Analytical Lab SOP O-019, *PIANO Volatiles by GC/MS*.

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

This method is applicable to the quantification and qualitative fingerprinting of petroleum products. If quantifying petroleum ranges using the individual n-alkanes, the reporting limit for the petroleum ranges is calculated by taking the sample concentration factor and multiplying it by the summation of the number of calibrated analyte(s) that elute in the range. The quantifying total petroleum ranges are generally $C_9$-$C_{44}$. Client specific ranges, as requested, are accommodated (*i.e.*, $C_{10}$-$C_{28}$, $C_9$-$C_{36}$, and $C_9$-$C_{40}$). The qualitative identification is dependent on the product pattern, how weathered it may be, and how much is present. This is the subjective aspect of the analysis that requires an experienced analyst. Care should be taken to ensure consistency in petroleum identification. Pattern books generated from the analysis of "typical" petroleum products (Section 8.12), analyzed under the same conditions as the samples may be used for reference.

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

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

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

# 2. Summary of Method

Please refer to the appropriate Alpha Analytical Lab SOPs for extraction methods and sample preparation information:

- *Method 3510C – Extraction of Water Samples by Separatory Funnel* (OP-001).
- *Shaker Table Extraction* (OP-013).
- *Tissue Preparation and Homogenization* (OP-003) and *Tissue Extraction* (OP-018)
- *Organic Waste Dilution* (OP-021)
- *Gravimetric Determination* (OP-017)

Analytes are introduced into the GC/FID by injecting a known volume of the calibration standards, quality control samples, and sample extracts into the GC equipped with a narrow-bore capillary column. The GC column is temperature programmed to separate the analytes, which are then detected with a flame ionization detector. Identification of target analytes is accomplished by comparing their retention time with the retention time of the calibration standards. Concentrations are determined using mean relative response factors from a multi-level calibration curve. Response factors for target analytes and surrogate compounds are determined relative to the internal standards. Typically, Petroleum Fuel/Hydrocarbon Ranges (TPH ranges listed by example in Section 1.0) are assigned the response factors (Rf) of the average of the calibrated n-alkanes and isoprenoids. The isoprenoids and the alkane n-Nonatriacontane (C39) are assigned the response factors (Rf) of the calibrated alkane eluting immediately after (for example the isoprenoid 1380 is assigned the response factor (Rf) of n-Tetradecane (C14). If defined by client or project data quality objectives (DQOs) or other specifications, sample concentrations may be measured by calibrating with a Diesel fuel or another site specific NAPL, or product. Sample quantification in these cases would be from the average Rf obtained from a multi-level calibration curve for the fuel product.

## 2.1 Method Modifications from Reference

The continuing calibration verification %D for each calibrated compound must be below 25%, with no more than 10% of all compounds greater than 25% but less than 35%. Each CCV must be analyzed within 24 hours of the previous CCV.

Matrix spike and duplicate samples are analyzed only if requested by the client.

# 3. Reporting Limits

Reporting limits for the individual n-alkane and isoprenoid are 200 mg/Kg (ppm) for petroleum products, 0.0667 mg/Kg (ppm) for soil/sediment samples, 0.267 mg/Kg (ppm) for tissue samples, and 0.001 mg/L (ppm) for water samples. Reporting Limits for DRO are listed on Table 1.

# 4. Interferences

**4.1** Contaminants in solvents, reagents, glassware, and other sample processing hardware may cause inferences that lead to discrete artifacts and/or elevated baselines in the chromatogram. Demonstrate that all of these materials are free from interferences under the conditions of the preparation and analysis by extracting and analyzing a laboratory method blank with each batch of up to 20 samples.

**4.2** Emulsions can form during the extraction especially in aqueous samples with high concentrations of petroleum contamination. This may require mechanical means to disperse such as glass stirring rods or centrifugation. Alternatively, filtration of emulsions through pre-dried sodium sulfate can be employed. Additional filtration through sodium sulfate after emulsion reduction is required to ensure adequate sample drying has been achieved.

**4.3** The injector system of the GC can become contaminated with non-volatile components from prepared samples, decreasing the resolution and responsiveness of the system. High molecular weight polyaromatic hydrocarbons (PAH) in the calibration mix can act as indicators of chromatographic problems. $C_{40}$ response decreases with increased injector contamination and is a good indicator compound. Maintenance of the analytical system should be performed when system performance degrades.

# 5. Health and Safety

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

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

# 6. Sample Collection, Preservation, Shipping and Handling

## 6.1 Sample Collection

Aqueous samples: Collected in pre-cleaned 1-L amber glass bottles.

Soil/sediment samples: Typically collected in a pre-cleaned 250ml soil jar with a teflon lined screw cap.

## 6.2 Sample Preservation

Aqueous samples: Stored without preservative and at 4°C.

Soil/sediment samples: Preserved by storing at 4°C.

## 6.3 Sample Shipping

No special shipping requirements.

## 6.4 Sample Handling

Aqueous samples: Extraction is performed within 7 days. Sample extracts are analyzed within 40 days of extraction.

Soil/sediment samples: Extraction is performed within 14 days of collection; extract is analyzed within 40 days of extraction.

There is no extraction holding time applied to petroleum product samples. If sediment samples are frozen, this suspends holding time until removal from the freezer. All extracts must be analyzed within 40 days of the extraction date.

# 7. Equipment and Supplies

**7.1 Gas Chromatograph** - The instrumentation includes a temperature-programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases. The injection port is designed for splitless injection onto a capillary column. The injection port includes a silanized glass liner containing a plug of silanized glass wool to reduce high-molecular-weight mass discrimination. The model is HP6890 or equivalent. The injector port will require maintenance on an as needed basis if degradation or contamination is apparent. Please refer to the front of the *Instrument Maintenance Logbook*, which outlines the routine maintenance procedures.

**7.2 Column** – Restek 60-m x 0.25 mm ID, 0.25um film thickness, fused-silica capillary column with RTX-5 bonded phase, or equivalent.

**7.3 Flame Ionization Detector (FID)** – The FID must operate at 20Hz data collection rate and have the attenuation optimized for signal to noise response. The GC capillary column is fed directly into the flame ionization detector. The FID will require cleaning and/or jet replacement on an as needed basis. Please refer to the instrument hardware manual for detailed procedures, located in the laboratory next to the instrument.

**7.4 Auto sampler** - Adapted onto the Gas Chromatograph. The model is HP 6890 series autosampler with a GC autosampler controller, or equivalent.

**7.5 Computer** - with Windows XP operating software utilizing HP Enviroquant G1701DA Version D.01.02 software or a more current release; Audit Trail: audit.txt function is used for audit trail purposes.

**7.6 Hydrogen** – Ultra high purity grade (99.9999% pure).

**7.7 Air** – Ultra Zero high purity grade (99.9999% pure).

**7.8 Helium** - Ultra Zero high purity grade (99.9999% pure).

**7.9 Glassware** - Assorted Class-A volumetric flasks consisting of 5mL through 200mL flasks with ground-glass stoppers for preparing reagents, standards, and measuring sample volumes for sample requiring dilution beyond 1:100.

**7.10 Pipettes:** Disposable Pasteur brand, or equivalent.

**7.11 Cahn balance:** Capable of accurate measurement to the nearest 0.001 mg.

**7.12 Analytical balance:** Capable of accurate measurement to the nearest 0.0001 g.

**7.13 Top-loading analytical balance:** Capable of accurate measurement to the nearest 0.1g.

**7.14 Micro syringes** - 10, 25, 50, 100, 250, 500, and 1000 µL.

**7.15 VOA vials:** Non-preserved, certified, pre-cleaned, 40 mL, with Teflon-lined screw caps.

**7.16 Vials, 2 mL:** with Teflon-lined crimp caps for standard solutions.

**7.17 Spatula** - Stainless steel.

# 8. Reagents and Standards

Use reagent grade chemicals for all reagents. Deionized (DI) water is ASTM Type II laboratory reagent grade water.

All stock standard solutions are purchased from commercial vendors as ampulated certified solutions or prepared in house from neat materials. Standards are stored according to the vendor recommendations. When an ampulated stock solution is opened, or prepared fresh from neat materials, it must be transferred into a PTFE-lined screw capped vial. Any extraction working standards are stored at -10 to -20°C, away from light, when not in use. All analytical working standard solutions are stored at room temperature. They are discarded after 1 year unless the vendor expiration date states otherwise or if breakdown is observed.

**8.1 Methylene Chloride:** ACS approved, Pesticide grade, see Alpha Analytical Lab SOP *Reagent, Solvent and Standard Control* (G-008) for additional details regarding solvent purity.

**8.2 Acetone:** ACS approved, Pesticide grade, see Alpha Analytical Lab SOP *Reagent, Solvent and Standard Control* (G-008) for additional details regarding solvent purity.

**8.3 Hexane:** ACS approved, Pesticide grade, see Alpha Analytical Lab SOP *Reagent, Solvent and Standard Control* (G-008) for additional details regarding solvent purity.

**8.4 Multi State Hydrocarbon Standard:** Obtained from Accustandard at 500ug/mL

**8.5 Internal Standard Calibration Stock:** 5-alpha-androstane neat from Sigma-Aldrich. Prepare a 10,000ug/mL solution by weighing 0.5g into 50mL of Methylene Chloride. Prepare a 1:20 dilution (2500ul into 50mL Methylene Chloride) for a 500ug/mL solution.

**8.6 Surrogate Stock:** Ortho-terphenyl neat from Sigma-Aldrich and n-Tetracosane-d50 neat from Cambridge Isotope. Prepare individual stocks at 20,000ug/mL each by weighing .5g into 25mL of Methylene Chloride. Prepare a 1:20 combined stock solution (5mL of each surrogate stock at 20,000ug/mL into 100mL Methylene Chloride) for a 1,000ug/mL solution.

**8.7 Surrogate Spiking Solution (SIS):** ortho-terphenyl and n-Tetracosane-d50 in a 20,000ug/mL stock solution prepared from neat. Prepare a solution by taking 2.5mL of each surrogate into 100mL of Methylene Chloride for a 500ug/mL spiking solution. The solution must be assayed for use by analysis before release to the preparation lab. All compounds must be within 10% of their true value. A manager's approval is needed for all surrogate spiking solutions before use. 100ul is spiked into each QC and field sample. This amount may be adjusted to meet project specific concentrations, as needed.

**8.8 Internal Standard (RIS):** 5-alpha-androstane in a 10,000ug/mL stock solution prepared from neat. Prepare a solution by taking 10mL into 200mL of Methylene Chloride for a 500ug/mL spiking solution. 100ul is spiked into each QC sample and field sample.

**8.9 Laboratory Control Sample, Matrix Spike, and Matrix Spike Duplicate (LCS/MS/MSD):** A solution of 14 alkanes from Ultra Scientific, or equivalent, at 1000ug/mL. This is a source separate from the calibration curve. Prepare a spike mix by adding 10mL of solution to 50mL of Methylene Chloride for a 200ug/mL LCS/MS/MSD spiking solution. The solution must be assayed for use by analysis before release to the preparation lab. All compounds must be within 20% of their true value. 100ul is spiked into each QC and field QC sample. This amount or component type may be adjusted to meet project specific concentrations, as needed.

**8.10 Alaska North Slope Crude Oil:** Neat. Weigh approximately 1.0g into 90mL of Methylene Chloride. To the 90mL add 10mL of the internal standard (RIS) for a stock solution of 50ug/mL.

**8.11 Independent Calibration Verification Standard (ICV):** A solution of all calibrated alkanes that are a separate lot from the calibration mixture can be obtained from Accustandard. The solution is prepared to the exact specs of the Continuing Calibration Verification standard.

**8.12 Petroleum Hydrocarbon Reference Standards:** These standards are used for a chromatographic library and qualitative identification. If requested, any of these petroleum standards may be used for instrument calibration or LCS Solution. All standards are diluted to be at a concentration of 5mg/mL for analysis when used as part of the Reference Library. The library should include but not be limited to standards of PAH, gasoline, jet fuels, kerosene, fuel oils, paint thinner, asphalt, lubricating oils, creosote, coal tar, cutting oil and hydraulic oil. Because reference materials cannot always be obtained as certified materials, the source of the reference standards should be documented (*i.e*. Fuel Oil #2 obtained from a particular fuel oil company on a particular date). Several reference standards can be obtained from Accustandard's complete list of Total Petroleum Hydrocarbon Recognition Standards.

# 9. Quality Control

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. Quality control exceedances are documented on the *TPH SHC Report Checklist (104-10)*.

## 9.1 Blank(s)

A method blank must be extracted (spiked with surrogates and internal standards) and analyzed once per every 20 samples or per extraction batch, whichever is more frequent.

Acceptance Criteria: Method Blanks should not contain any individual compound at or above the concentration of the reporting limit. If a blank does contain target compounds greater than the reporting limit, they should be less than 20% of any sample results for the same compound(s). Individual compounds may be detected in the blank below the reporting limit. Associated sample results are flagged with a “B” qualifier if the concentration of the analyte in the sample is less than 5x the concentration in the blank.

Corrective Action: If the blank does not meet the above criteria, all efforts must be made to identify and eliminate any source of contamination, and all samples associated with the contaminated blank should be re-extracted and reanalyzed. Exceptions may be made with the approval of the Department Manager. Any exceedances are noted in the case narrative.

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

The LCS spike is from a second source, and can additionally be used to verify the accuracy of the standard curve. The LCS spiking solution is a mixture of 14 n-alkanes spread over the $C_9$ to $C_{40}$ calibration range. The LCS and LCSD are extracted along with the samples as a measure of precision and accuracy. At a minimum, one LCS/LCSD must be analyzed at a frequency of once per 20 samples, or per analytical batch, whichever is more frequent.

Acceptance Criteria: All LCS compound recoveries must be between 50-130% of the true values. The acceptable recovery QC limits are found in Section 12 for aqueous, solid, tissue, and product LCSs.

Corrective Action: Repeat analysis once to see if an analytical error has occurred. If the LCS/ LCSD % RPD or % Recovery is still out of the control limit check the sample archive. Samples cannot be analyzed until an acceptable LCS is obtained. The samples associated to the LCS/ LCSD may need to be re-extracted. Exceptions may be made with approval of the Section Head if the samples associated with the out of control LCS/ LCSD are also associated with a MS/MSD pair that is in control. This is an acceptable measure of precision and accuracy of the analytical procedures. An explanation of this out of control LCS/LCSD recovery must be included in the project narrative to the client and the sample data reported noting the acceptable MS/MSD results as the batch QC.

## 9.3 Initial Calibration Verification (ICV)

The analysis of an ICV standard must follow the initial calibration curve.

After final processing, calculate the percent recovery of each n-alkane and isoprenoid by using the following calculation:

**% Recovery = Found Amount / True Value x 100**

Acceptance Criteria: All recoveries must be +/- 20% of the true values.

Corrective Action: If the initial calibration fails, perform instrument maintenance and repeat.

## 9.4 Continuing Calibration Verification (CCV)

A continuing calibration verification (CCV) standard, at the concentration of a mid-level initial calibration standard, must be analyzed at the beginning and end of every analytical sequence, and every 24 hours within the sequence, to confirm instrument stability, via response factor, for each calibrated n-alkane.

Acceptance Criteria: Compare the CCV resulting response against the average response for the initial calibration for each calibrated n-alkane and isoprenoid. The %D for each calibrated compound must be below 25%, with no more than 10% of all compounds greater than 25% but less than 35%. If multiple CCVs are analyzed within an analytical sequence, each CCV must be analyzed within 24 hours of the previous CCV. Each CCV, including the ending CCV must meet the acceptance criteria. The acceptable QC limits are found in Section 12.

Corrective Action: If the CCV does not meet the acceptance criteria for each calibrated n-alkane and isoprenoid, perform instrument maintenance and repeat the continuing calibration. Re-analyze all affected samples. Reported results for the failing CCV may be “J” qualified. If the failure of the suspect response appears related to a loss in FID sensitivity, instrument maintenance and repeat analysis of the continuing calibration, and all affected samples, must be performed. Exceptions may be made with the approval of the Department Section Head. Any exceedances are noted in the case narrative.

## 9.5 Matrix Spike / Matrix Spike Duplicate (MS / MSD)

Matrix spike samples are analyzed only if requested by the client. Matrix duplicate analyses (as an MS/MSD pair) can be performed once per 20 samples (5% frequency) at the clients' request. It is preferable to extract samples that have been selected specifically by the client. If none have been assigned, then the laboratory analyst must choose a representative sample for each type of matrix prepared. Aqueous duplicates can only be done if the client supplies sufficient sample. These samples are also spiked with extraction surrogate.

Acceptance Criteria: All matrix spike compound recoveries must be between 50-150% of the true values. The acceptable recovery QC limits are found in Section 12 for an aqueous, solid, tissue, and product matrix spike analysis.

Acceptable relative percent difference (RPD) for matrix spike analysis is ± 30 % for both aqueous and solid matrices. Acceptance criterion is not applicable to sample concentrations less than 5 times the reporting limit. Calculate RPD as follows:

$$RPD = \frac{R1 - R2}{\frac{[R1 + R2]}{2}} \times 100$$

Corrective Action: Repeat analysis once to see if an analytical error has occurred. If the % RPD or % Recovery still exceeds the control limits and the LCS/ LCSD is compliant; include a project narrative with the results to the client noting that there may be potential matrix effects on the precision of the affected results as evidenced by the MS/MSD recoveries or %RPD outside of QC limits.

## 9.6 Laboratory Duplicate

Acceptance Criteria: Laboratory matrix or sample duplicates are analyzed if requested by the client. The QC limit is 30% RPD for target compounds found above 5 times the reporting limit.

Corrective Action: If the %RPD exceeds the 30% control limit and the associated MS/MSD %RPD is within 30%, include a project narrative with the results to client noting that there may be potential matrix effects on the precision of the results isolated to this sample, as evidenced by the matrix duplicate exceedence and the MS/MSD acceptance. If both the sample/duplicate and the MS/MSD exceed the control limits, include a project narrative with the results to client noting that there may be potential matrix effects on the precision of the results as evidenced by the sample/duplicate and the MS/MSD exceedences.

## 9.7 Method-specific Quality Control Samples

### 9.7.1 Surrogates

Acceptance Criteria: All surrogate recoveries must be between 50-130% of the true values. Surrogates are monitored for percent recovery for all matrices. The recovery limits are found in Section 12.

Corrective Action: If the surrogate does not fall within the QC limits, check to be sure there are no errors in peak integration, calculations, and surrogate solutions. If only one surrogate falls below the 50% recovery limit, the exceedence is noted, with approval of the Department Manager, and the results are reported to the client with a notation in the case narrative. If all surrogates are recovered below the 50% limit, re-extract the sample and report the re-extract results along with the original results, if re-extraction occurred beyond the holding time, and the re-extract surrogates are within the QC limits. If the surrogates are recovered below 50% in the re-extract, this confirms a suspected matrix interference on the surrogates, and only the original analysis needs to be reported. If the chromatogram shows obvious matrix interference, no re-analysis or re-extraction is necessary. *This decision must be made with approval of the* Department Manager. Surrogate outliers and sample re-extracts must be noted in the case narrative to the client.

### 9.7.2 Internal Standards

Acceptance Criteria: Internal standards are added to every field sample, QC sample, standard, and method blank. The acceptance limits are 50-200% of the internal standard response (or area) of the daily continuing calibration verification standard.

Corrective Action: Check to see if an analytical, dilution or spiking error occurred. If the chromatogram shows obvious matrix interference, no re-analysis is necessary. This decision must be made with approval of the Department Manager. Note the exceedence in the case narrative to the client. If no obvious interference is present, re-analyze the extract. If internal standards are now within the acceptance limits, report only the re-analysis, as long as the re-analysis occurred within the 40-day analytical hold time. If the re-analysis occurred outside of the 40-day analytical hold time, both the original and re-analysis must be reported. If the internal standards

again are outside the acceptance limits, after re-analysis, either within or outside of the 40-day hold time, report only the original analysis, and include a narrative to the client that the suspected matrix interference on the internal standards was confirmed by sample re-analysis.

## 9.8 Method Sequence

Samples are prioritized for analysis by the Department Manager or Team Leader based on client due date and sample analytical hold time. Samples are retrieved from the sample storage refrigerator.

The sequence is prepared and run using the Enviroquant software. Printouts of all sequences are kept in a three-ring notebook for each instrument. The sequence printouts are used to document run sequences; notations are manually added of any reruns or dilutions that will need to be performed in the daily SHC continuing calibration verification packages.

- Instrument Primer
- Continuing Calibration Verification (CCV)
- Instrument Solvent blanks
- Method Blank
- Laboratory control samples (LCS/LCSD)
- Samples (1-10)
- Continuing Calibration Verification (CCV)

# 10. Procedure

Prior to performing Total Petroleum and Saturated Hydrocarbon GC/FID analysis, the operator must read and become familiar with the operating procedure guidelines specified in the instrument operating manuals. The analyst must be trained and familiarized with the instrument software provided by the manufacturer. The instrument must be set up with the proper operating parameters (data acquisition and processing) and conditions described in the operating manual. The criteria for the analytical calibration ranges and method and instrument detection limits must be established and documented prior to initial calibration.

All samples and standard solutions must be allowed to warm to ambient temperature before analysis.

## 10.1 Equipment Set-up

### 10.1.1 GC Instrumental Conditions

Inject a 1uL aliquot of sample extract or standard solution into the capillary column of the gas chromatograph at the following conditions.

| GC Parameter | Setting |
|---|---|
| Injector Temp: | 280 °C |
| Initial Oven Temp: | 40 °C |
| Initial Hold Time: | 1 minute |
| Column Flow: | 3.0 mL/ minute |
| Ramp Rate: | 6 °C / minute |

| | |
|---|---|
| Final Temperature: | 315 °C |
| Final Hold Time: | 30 minutes |
| Total runtime: | 76.83 minutes |
| Mode: | Pulsed Splitless |
| Pulse: | 15psi for 0.8 minute |
| Purge: | 20 mL / minute – on at 1.0 minutes |
| FID Temperature | 325 °C |

## 10.2 Initial Calibration

| | Volume added | | | |
|---|---|---|---|---|
| **Calibration Level** | **Alkane Standard** | **Surrogate Stock** | **Internal Standard Stock** | **Final Volume in Methylene Chloride** |
| Level 1 -1ug/mL | 20ul | 10ul | 1000ul | 10mL |
| Level 2 -10ug/mL | 200ul | 100ul | 1000ul | 10mL |
| Level 3 -50ug/mL | 5000ul | 2500ul | 5000ul | 50mL |
| Level 4 -100ug/mL | 2000ul | 1000ul | 1000ul | 10mL |
| Level 5 -200ug/mL | 4000ul | 2000ul | 1000ul | 10mL |
| Level 6 -500ug/mL | NA | 5000ul | 1000ul | 10mL |
| SHC - ICV | 1000ul | 500ul | 1000ul | 10mL |

**10.2.1** Before analysis of sample extracts, establish a multi-point response factor calibration curve showing the linear range of the analysis for all individual target analytes. Use standard concentrations of 1, 10, 50, 100, 200 and 500, ug/mL to construct the curve. See Section 8 and Table above for the preparation of the standard solutions for the initial calibration curve. Conversely, and if project specifications require, a minimum 5 point calibration curve may also be constructed using a specified fuel product of interest. The calibration range, and thus the reporting limit for this type of calibration, is several factors higher than for the individual component calibration. A Fuel Product calibration curve is typically 100ug/mL to 50,000ug/mL. Section 8.12 lists fuel products typically used.

**10.2.2** Run a sequence with the initial calibration standards.

- Create a processing method from a previous method on that instrument. Set retention time windows using a mid level standard.
- Quantitate and QEDIT the initial calibration standards. Update the method with these standards.
- Additionally, the response for the petroleum ranges must be hand entered. The average area of all individual components is used to calculate the Rf for the petroleum ranges. The ranges are typically specified by the client or project DQOs. **NOTE**: It should be noted that quantification of a Fuel Product Range using the Rf generated from individual n-alkanes can lead to a *20% - 30% low bias* of the reported TPH range.
- To avoid the low bias discussed above, calibration of the Fuel Product of interest is recommended. The product of interest should be prepared at five concentrations, as

in 10.2.1 above, to construct a calibration curve, integrated for the range of interest, which is typically specified by the client. The resulting average Rf for the fuel of interest is used to quantify the associated field samples. Typical fuel products are listed in Section 8.12. Calculations are found in Section 11.0.

Acceptance Criteria: 25% RSD for all individual target compounds and 20% RSD for fuel products. All calibration standards must be analyzed within 24 hours.

#### 10.2.3 Initial Calibration Verification (ICV)

- The analysis of an ICV standard must follow the initial calibration curve.
- After final processing, calculate the percent recovery of each compound by using the following calculation:

**% Recovery = Found Amount / True Value x 100**

- Acceptance Criteria: All recoveries must be +/- 20% of the true values.
- ICALs are documented on the *TPH SHC Initial Calibration Checklist (104-09)*. The initial calibration must be secondary reviewed before analyzing samples

The following *corrective actions* are recommended for failing initial calibrations:

- Check the calibration of the standard preparation that was performed. If the problem appears to be isolated to a single standard, the standard may be reanalyzed within twelve hours. The %RSD may then be recalculated.
- If chromatographic problems are indicated by the standard chromatograms already analyzed, then the injection port should be maintenanced. About 6 to 12 inches should be cut off the column, and the liner should be replaced. If applicable the septa should also be replaced. If the system continues to fail after maintenance and has poor sensitivity it is possible the detector jet may need to be cleaned or replaced. The gold seal at the base of the injection port may also need to be replaced. After maintenance is performed repeat the initial calibration and check the re-calculated %RSDs.
- If calibration continues to fail, determine if the column is worn out and should be replaced. The choice of corrective active must be made in consultation with the Department Manager. In some cases the decision may need consultation from the QA Manager and Project Manager.

## 10.3 Equipment Operation and Sample Processing

Instructions on equipment operation and data processing can be found in the Agilent Enviroquant manuals. Operation of equipment and sample processing must only be performed by experienced and trained analysts. See Sections 10 and 11 for additional details.

The internal standard (100uL of a 500ug/mL solution to 900uL extract) is manually added to each sample extract prior to analysis. A 1ul aliquot of sample extract is injected into the column. Dilutions may be necessary to provide results within the calibration of the analytical instrument. The internal standard should be within the control limits listed in Section 12.0. If the IS is outside this criteria; reanalyze. If the reanalysis confirms the initial analysis, then the results are reported and narrated appropriately.

Surrogate recoveries should be within the control limits listed in Section 12.0. If any surrogate recoveries are outside the control limits reanalysis or reextraction may be necessary. Any anomalous conditions, such as emulsions during extraction or matrix interference, could be the

cause of poor surrogate recoveries. If these conditions occur, then the results are reported and narrated appropriately.

## 10.4 Continuing Calibration

The systems performance and calibration for each compound of interest must be checked and verified once every 24 hours of analysis time. This is accomplished by analyzing a Continuing Calibration Verification (CCV) n-alkane standard that is at a concentration near the midpoint for the working range of the GC/FID, 50µg/mL.

- Analysis of samples must be bracketed by a valid continuing calibration check standard.
- If a CCV fails the criteria outlined in Section 12, all samples since the last acceptable CCV must be re-analyzed.
- The analyst judgment from continuous daily use of the instrument is important in determining the validity of a continuing calibration. Even if the %D criteria is met, the peak shape may have deteriorated to a point of maintenance is required and a new initial calibration is in order.
- A low response for $C_{40}$ is an indication that the GC liner should be replaced.
- When analyzing for extended lists of hydrocarbons, the ratio of phytane to n-$C_{18}$ must be 60% or better for the test to appropriately provide weathering information. If the ratio is acceptable, it is assumed that the n-$C_{17}$ to pristane ratio is also acceptable.
- The ratio of $C_{36}$ to $C_{20}$ should not be less than 0.85 and more than 1.15.
- All CCVs are documented on the *TPH SHC Continuing Calibration Checklist (104-08)*.

## 10.5 Preventive Maintenance

All maintenance records including routine upkeep and outside service visits are maintained in the instrument maintenance logbooks for all FID systems. The maintenance logbook contains the minimum preventative maintenance and a history of all instrument maintenance. The instrument operating manuals provide more detailed information. These instruments are NOT under a maintenance service contract with the vendors. For repairs beyond the scope of routine upkeep and preventative maintenance, an independent service contractor must be called for on-site service and repairs.

**Injection Port and Column Maintenance:** Maintenance should be done when the daily CCV starts to demonstrate degradation. The type of samples analyzed will have an effect on how soon maintenance should be performed. The injection port can be cleaned using cotton swabs and DCM until no contamination is observed. Generally maintenance is performed by trimming 6 cm off the front of the column. The column is then installed into the injection port liner and the inlet nut is tightened. After cleaning the instrument must be checked for any air leaks while cooling. The first injection should be a primer to remove any active sites and to check if any of the windows need updating.

**Merlin Maintenance:** The Merlin High Pressure Microseal (Part #410 Phenomenex) should be replaced when it cannot hold back pressure. A septum may be used as a backup or for troubleshooting.

# 11. Data Evaluation, Calculations and Reporting

**11.1** Qualitative Identification of the n-alkane compounds is based on gas chromatographic relative retention times (RRTs) from the analysis of the mid-level initial calibration standard. For these compounds, manual quantitations are performed, if necessary, by integrating the area of the quantitation peak. For *petroleum ranges*, the starting and ending n-alkanes are used as integration markers.

**Note:** Manual integration is not to be used solely to meet QC criteria, nor is it to be used as a substitute for corrective action on the chromatographic system. Refer to the Manual Integration SOP 08-03.

**11.2** In instances where manual integration has been performed, the analyst must initial and date the quantitation report.

**11.2.1** An Instrument Blank run within the analytical sequence with the samples shall be used to mathematically correct the range analyte areas to account for the normal baseline rise of the instrument. The instrument blank selected for this purpose will be selected on 1) the similarity of the baseline performance between the instrument blank and the sample, and 2) the conservative preference for using an instrument blank with a low minimum response voltage. The instrument blank for baseline correction shall represent the lowest baseline response within the sequence. The blank is integrated for petroleum ranges only. This integration is then applied to the samples so an identical amount of baseline drift is removed from the sample leaving only petroleum contributions in the range amount.

**11.2.2** The chromatograms produced by the analysis are compared to reference chromatograms for qualitative identification. The reference chromatograms are stored as hard copy results as well as electronically in the data acquisition software. Electronic storage allows for evaluation using computer software.

**11.2.3** The qualitative analysis can be time consuming. Retention time information for the alkanes and any Unresolved Complex Mixtures is essential. The graphical comparison of sample patterns to standard patterns is extremely useful in the interpretation of results. For example a low range UCM may indicate the presence of a petroleum based lubricant. A mid range UCM may indicate the presence of fuel oil. High range UCM may indicate heavy lubricating oils or asphalt materials. No UCM in a chromatogram may indicate the presence of gasoline. Hard copy reports of comparisons should be retained for future reference.

**11.3** To calculate the ***Relative Standard Deviation*** (RSD) of all target analytes and surrogate compounds for the initial calibration use the formula below. The RSD of each target compound and surrogate must be below 25%. Additionally, use the initial six-point calibration to determine ***Relative Response Factors*** ($RRF_I$s) at each concentration level. Average the $RRF_I$s, to generate mean $RRF_I$s, for quantification of all target analytes and surrogate compounds. The $RRF_I$s are based on the internal standard compounds, and are calculated using the formula below. (The relative response factors for the continuing calibration verifications ($RRF_C$s) are calculated using the same formula). See Section 16, Table I, for the listing of target compounds and their associated internal standards for quantification.

$$\mathbf{RSD = SD \ / \ mean\ RRF_I \ x \ 100}$$

where:

SD = Standard deviation between the five points, for that target analyte.

$$RRF_I = (A_c \times C_{IS}) / (A_{IS} \times C_c)$$

where:

$A_c$ = Area of the characteristic ion for the standard compound to be measured.
$A_{IS}$ = Area of the characteristic ion for the representative internal standard compound.
$C_{IS}$ = Concentration of the representative internal standard compound (ng/mL).
$C_c$ = Concentration of the standard compound to be measured (ng/mL).

**11.4** Based on the mean $RRF_I$s, calculate the ***Sample Extract Amount*** for each target analyte and surrogate in the extracts using the following formula:

$$Q_e = (A_a \times Q_{IS}) / (A_{IS} \times RRF_I)$$

where:
$Q_e$ = Sample extract amount (ng) of target analyte, from quantitation report.
$A_a$ = Area of the characteristic peak for the target analyte.
$A_{IS}$ = Area of the characteristic peak for the representative internal standard compound.
$Q_{IS}$ = Amount of internal standard compound added to each extract (ng).

**11.5** Based on the area calculate the **Corrected Range Amount** for the petroleum ranges:

$$Q_e = ( (A_{SR}-A_{IB})/A_{SR})*C_S$$

where:

$Q_e$ = Corrected sample extract amount (ng) of petroleum range.
$A_{SR}$ = Area of the sample petroleum range.
$A_{IB}$ = Area of the Instrument Blank petroleum range.
$C_S$ = Sample extract amount for petroleum range, from quantitation report.

The corrected range amount is then brought through the sample calculation found in Section 11.6

**11.6** Calculate the ***Sample Concentration*** (C) for each compound by the following formula:

$$C = (Q_e / V_s) \times DF$$

where:

C = Concentration in sample (ng/L water, ug/Kg sediment/tissue, or mg/Kg product).
$V_s$ = Original volume or weight of sample extracted.
DF = Dilution factor or fraction of the original extract to which internal standard added.

**11.7** If the response of any target compound in a sample exceeds the linear response range, as defined by the initial calibration standards in Section 10.2, dilute the extract so that the concentrations of all target compounds fall within the range of the calibration curve. If the response of any target compound in a sample exceeds the MDL but is below the reporting limit (RL), qualify the reported concentration with a “J”. If any target compound is found in the method blank and in the associated sample(s) at or below 5x the blank concentration, qualify the reported result with a “B”.

**11.8** Calculate the ***Surrogate Recoveries*** relative to the internal standards by the following formula:

$$\%R_{sc} = (A_{sc} / A_{is}) \times (Q_{is} / Q_{sc}) \times (100 / RRF_{sc}) \times DF$$

where:

$Q_{is}$ = Amount of the representative internal standard (ng).
DF = Dilution factor or fraction of the original extract.

**11.9** Compare response factors for each compound in the ***Continuing Calibration Verification*** (CCV), to those of the initial calibration curve by determining the percent difference.

$$\text{Percent Difference (\%D)} = ([RRF_I - RRF_C] / RRF_I) \times 100$$

where:

$RRF_I$ = Mean response factor from initial calibration.
$RRF_C$ = Response factor from CCV.

**11.10** External Standard Calibration:

$$\text{Calibration Factor (CF)} = \frac{\text{Total area w/in RT Range}}{\text{Mass injected (ng)}}$$

$$\%RSD = \frac{SD}{\text{Ave. CF}} \times 100$$

$$\text{Raw Sample Concentration, C, (ng)} = \frac{\text{Total area w/in RT Range}}{\text{Ave. CF}}$$

$$\text{Final Sample Concentration} = (C / V_s) \times DF$$

**11.11** All solids including soils, sediments, and sludges must be reported on a dry-weight basis. Tissue results may be reported in wet-weight depending upon client request. Petroleum results are reported “as received” or on a wet-weight basis.

**11.12** The primary analyst does data entry, or uploading of the data, into the LIMS system. The LIMS is “linked” to the instrument, so the analyst must choose the sample(s) to be reported from that instrument’s analytical sequence. All associated preparation and instrumental QC samples and dilutions are also chosen. Once the data/samples have been selected and “associated” with the proper QC samples, the batched data set is sent to be reported.

**11.13** The laboratory generates two types of data packages from the LIMS: “Commercial” or “Standard” for routine projects, and “Full Deliverable” or “CLP-like” for fully data validated projects. A Commercial or Standard package consists of sample results and the associated method blank and LCS results. A Full Deliverable or CLP-like package includes all sample results, all preparation and instrumental QC results and the associated supporting raw data. Check the “Report Type” on the project folder to ensure all required deliverables are included. Checklists are used for primary and secondary review of the analytical results.

**11.14** Procedures for data and record management must adhere to the Quality Systems Manual, other subordinate documents covering record keeping, and the *Document Control* SOP, 08-01. All records shall be stored in such a manner as to be safe and accessible for at least 10 years.

**11.15** Notebooks: Laboratory notebooks are designed to accommodate the specific analysis. Instrument printouts are used to document run sequences, and each daily sequence printout is filed in a three-ring notebook. If a sample requires re-analysis or re-extraction for any reason, a notation is made next to the sample entry on the sequence log in the FID continuing calibration package. Requests for re-extraction are further documented in the "Request for Re-extraction" logbook. After one month of sample analysis, the sequence run log is permanently bound, assigned an internal ID number, and filed accordingly. Such files shall be archived so as to remain available for at least 10 years. All laboratory notebooks must follow the specifications in the Laboratory Notebook Usage Work Instructions WI/108-01, and all record keeping and document control practices.

**11.16** Electronic records: All data files from computers, attached to instruments, shall be backed up daily onto the proper directory on the server. The backups shall be stored so as to be accessible for 10 years. Movement of the data files to the server is the responsibility of the primary analyst. Server backup and storage is the responsibility of the IT department.

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

All Total Petroleum Hydrocarbon results are reportable without qualification if analytical holding times are met, preservation (including pH and cooler temperatures) are met, and all QC criteria defined in the table below are met. If any of the below QC parameters are not met, all associated samples must be evaluated for re-analysis. See Section 9 for additional QC discussion including corrective actions for any QC outliers.

| QC Parameter | Acceptance Criteria |
|---|---|
| Initial Calibration Curve | ≤ 25 %RSD for the all compounds and within 0.06 RRT units for all compounds<br>Fuel Product: ≤20% RSD |
| 24 Hour Continuing Calibration Verification | ≤ 25%D for all individual compounds with exception for 10% of target analytes can be >25%, but ≤ 35%<br>Fuel Product: ≤20%D |
| Method Blank | No analyte at or above the reporting limit, "B" qualify analyte if detected in the samples ≤ 5x the concentration in the blank |
| LCS/LCSD | 50-130% recovery |
| MS/MSD | 50-150% recovery, 30%RPD |
| Matrix Duplicate | 30%RPD for results >5X reporting limit |
| Surrogates | 50-130% recovery |
| Internal Standards | IS area must be within 50-200% of the last CCV and the IS retention time must be with 30 seconds of the last CCV. |

Section 9 outlines sample batch QC acceptance criteria. If non-compliant Total Petroleum Hydrocarbon results are to be reported, the Department Manager, and/or the Laboratory Director, and/or the QA Officer must approve the reporting of these results. The laboratory Project Manager shall be notified, and may chose to relay the non-compliance to the client, for approval, or other corrective action, such as re-sampling and re-analysis. The analyst or Department Manager

performing the secondary review initiates the project narrative, and the narrative must clearly document the non-compliance and provide a reason for acceptance of these results.

# 13. Method Performance

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

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

## 13.2 Demonstration of Capability Studies

Refer to Alpha SOP/08-12 for further information regarding IDC/DOC Generation.

### 13.2.1 Initial (IDC)

The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method, prior to the processing of any samples.

### 13.2.2 Continuing (DOC)

The analyst must make a continuing, annual, demonstration of the ability to generate acceptable accuracy and precision with this method.

# 14. Pollution Prevention and Waste Management

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

Once satisfactory Petroleum results have been generated, the extracts are held for 30 days, or longer if specified by a client contract, then discarded into a 55-gallon drum labeled "Vial Waste".

# 15. Referenced Documents

Chemical Hygiene Plan

SOP/08-01 Document Control

SOP/08-03 Manual Integration

SOP/08-05 MDL/LOD/LOQ Generation

SOP/08-12 IDC/DOC Generation

SOP/G-006 Waste Management and Disposal SOP

SOP/G-008 Reagent, Solvent and Standard Control

SOP/O-019 PIANO Volatiles

SOP/OP-001 Separatory Funnel

SOP/OP-003 Tissue Preparation and Homogenization

SOP/OP-013 Shaker Table Extraction

SOP/OP-017 Gravimetric Determination

SOP/OP-018 Tissue Extraction

SOP/OP-021 Organic Waster Dilution

# 16. Attachments

Table I: Reporting Limit for DRO.

**Table I**

**Reporting Limit for DRO**

| Compound | Aqueous in mg/L | Solid in mg/Kg |
|---|---|---|
| **Diesel #2** | **1.0** | **100** |