TEXAS NATURAL RESOURCE CONSERVATION COMMISSION

TOTAL PETROLEUM HYDROCARBONS
TNRCC Method 1005
Revision 03
June 1, 2001

Jeffrey A. Saitas, P.E.
Executive Director

Revision 03
June 2000

TNRCC Method 1005, Rev 03, allows for some method modification based on project objectives. The general information provided below is followed by additional PST program-specific guidance.

For general information and clarification applicable to the 30 TAC 334, 335, and 350 rules

- As of June 1, 2001, all TPH data used under the above rules should be generated using TNRCC Method 1005, Rev 03. Analytical TPH data generated using EPA Method 418.1 or SW846-8015 will not be accepted if the analysis date on the reported TPH result(s) is after September 1, 2001. Other program areas within the TNRCC, such as the wastewater program area, may require TPH analysis by a method other than TNRCC Method 1005.

- To clarify Section 6.1, solid samples collected for TPH analysis should be placed on wet ice immediately after collection and held at 4 degrees C or lower. Upon receipt in laboratory the samples can be held at 4 degrees C or lower if the laboratory can analyze the samples within 2 days from the time of collection. Otherwise, the samples should be placed in a properly maintained freezer until extracted and analyzed.

- The laboratory does not need to calibrate the instrument for the >nC28 to nC35 boiling point range. It is acceptable to use the response factor derived from the 1:1 gas/diesel calibration curve for this boiling point range.

- When existing data or knowledge can be used to document no hydrocarbons are present > nC28, the analysis(es) can be truncated just after the nC28 marker.

- If existing data or knowledge can be used to document no hydrocarbons are present between nC6 and nC12, then the sample(s) can be collected using the bulk sampling technique, i.e., the sample is transferred from the medium into a 4-ounce jar (with a Teflon™-lined lid) filling the sample container as full as possible to minimize the head space.

- TPH data used to meet waste classification criteria should be reported on a dry weight basis including the percent solid results.
- If the laboratory reported quantified results from nC6 to nC10, instead of nC6 to nC12 for sample data generated before June 1, 2001, the laboratory can review the chromatogram(s) and provide an estimate of the hydrocarbons detected between the nC6 and the nC12 markers and the nC12 and nC28.

- The justification for using any method-allowed modifications should be documented and kept on file.

- If the project objectives have not been defined, or if no existing data or knowledge can be used for the affected medium, and/or if the person or the laboratory does not know how the data are to be used or under which rule the data will be submitted to the agency, then it is recommended the laboratory and/or the person make no modification to the method and report the data as recommended in the method to ensure the greatest possible use of the data under any of the

programs. For example, if no data are available to document hydrocarbons are not present beyond the nC28 boiling point, then the results should be reported out to the nC35 boiling point.

Under the **30 TAC 334 rule**, i.e., the Petroleum Storage Tank (PST) rule, the following method-allowed modifications should be made to TNRCC Method 1005, Revision 03. With these modifications, no additional reimbursable costs are warranted. These modifications are acceptable because the PST program only uses TPH data qualitatively for screening purposes to determine when a polynuclear aromatic hydrocarbon (PAH) analysis should be performed. No cleanups are based solely on TPH levels.

In Section 5.2 - Only the surrogate compound for the >nC12 boiling point range is needed for the analysis.

In Section 6.0 - Sample collection using SW846-5035 techniques is not required. Solid samples can be collected using a bulk sampling method, i.e., the sample is transferred from the medium into a 4-ounce jar (with a Teflon™ lined lid) filling the sample container as full as possible to minimize the head space.

In Section 7.2 - The chromatographic run can be stopped just after the retention time window of the nC28 marker, but the laboratory must indicate in the report whether hydrocarbons were present in the >nC28 range.

In Section 9.1 - If the intended use of the sample data does not include waste classification, the results for solid samples can be reported by the laboratory on an as-received (or wet weight) basis instead of on a dry weight basis. However, if the results are to be used to classify wastes, the results for solid samples should be reported on a dry weight basis and include the percent solid results.

If the laboratory reported quantified results from nC6 to nC10, instead of nC6 to nC12 for sample data generated before and/or on June 1, 2001, the laboratory or consultant can review the chromatogram(s) and provide a qualitative assessment in its case narrative documenting whether the results indicate no hydrocarbons were detected >nC12. This information can be used to demonstrate a PAH analysis is not warranted for the sampled area. Otherwise, if hydrocarbons are detected in the >nC12 range, a PAH analysis should be performed.

TOTAL PETROLEUM HYDROCARBONS
TNRCC METHOD 1005

Revision: 03 **Supercedes:** Revision 01, 02, and
Effective Date: June 1, 2001 Revision 4/13/98

1.0 PURPOSE AND APPLICATION

1.1 Scope and Application

This method is designed to determine total concentrations of petroleum hydrocarbons (TPH) in solid and aqueous matrices using gas chromatography. This method can be used for the quantitative analysis of petroleum hydrocarbons in the gasoline and diesel ranges and portions of the heavier fuel and lubricating oil range, which have approximate boiling points between n-hexane (nC_6) and n-pentatriacontane (nC_{35}). The analysis may be truncated at n-octacosane (nC_{28}) when the environmental medium of concern, or the suspected source of the TPH, does not contain hydrocarbons in the heavier hydrocarbon boiling point range, i.e., $>nC_{28}$ to nC_{35}.

The analytical results from this method may be correlated to those results generated using EPA Method 418.1. The persons should ascertain from the regulatory entity as to whether TNRCC Method 1005 analysis can be used in lieu of analysis by EPA Method 418.1.

The results from this method are used to measure the concentration of TPH in affected environmental media and to evaluate the relative distribution of the petroleum hydrocarbons in the TPH mixture. The laboratory includes n-alkane markers, e.g., nC_6, n-dodecane (nC_{12}), nC_{28}, and $nC_{35,}$ in the analysis to aid the data user in reviewing the chromatographic profile to evaluate the distribution of the hydrocarbons in the TPH.

> NOTE: If specified by the data user, other n-alkane markers, such as those markers specified in TNRCC Method 1006, can be used in this method.

This method is not intended for the quantitation of individual target analytes, such as benzene, toluene, ethylbenzene, and xylene (BTEX) and polynuclear aromatic hydrocarbons (PAHs). Those target analytes are best determined by EPA Methods SW846-8260, SW846-8021, and SW846-8270, where appropriate.

This method is a gas chromatography (GC) method with flame ionization detection (FID). The GC method is used to separate the TPH into two ranges (nC_6 to nC_{12} and $>nC_{12}$ to nC_{28}), and a third range ($>nC_{28}$ to nC_{35}) when applicable, based on boiling points of the hydrocarbons. The response of the FID is generally equal for all hydrocarbons on a weight basis. The method quantitation limit for TPH using this method is estimated to be 50 mg/kg in a solid matrix and 5 mg/L in an aqueous matrix depending upon the number of hydrocarbons present in the nC_6 to nC_{35} range.

This method should be used by, or under the supervision of, analysts experienced in the use of solvent extraction and gas chromatography. The analysts should also be skilled in the interpretation of capillary gas chromatography data (specifically petroleum hydrocarbon pattern recognition), quantitation using computerized data acquisition, and the use of peak processing software with baseline and peak grouping functions.

The quality assurance program of the laboratory generating the data should be documented and should be generally consistent with the National Environmental Laboratory Accreditation Conference (NELAC) standards which can be accessed at http://www.epa.gov/ttn/nelac.

2.0 SUMMARY OF METHOD

This method is an n-pentane extraction followed by gas chromatography/flame ionization detection (GC/FID) analysis which measures the concentration of hydrocarbons between nC_6 and nC_{35}. The method uses a 1:1 mixture of commercially available unleaded gasoline and diesel #2 fuel as calibration standards and the n-alkane markers, nC_6, nC_{12}, nC_{28} and nC_{35}, to establish the boiling point range boundaries. However, single hydrocarbon components can be used for calibration standards.

Generally, results are reported for boiling point ranges nC_6 to nC_{12}, $>nC_{12}$ to nC_{28}, and $>nC_{28}$ to nC_{35}. The concentration of TPH is reported as the summation of all carbon ranges, i.e., nC_6 to nC_{35}. Alternatively, when requested by the data user prior to analysis, the results can be generated and reported using the same hydrocarbon markers as found in TNRCC method 1006.

> NOTE: The analysis can be truncated at nC_{28} when it can be demonstrated that the environmental medium of concern, or the suspected source of the TPH, does not contain hydrocarbons in the heavier hydrocarbon boiling point range, i.e., $>nC_{28}$ to nC_{35}.
>
> NOTE: If the laboratory is unable to find a vendor for an nC_{35} standard, the laboratory should use an n-hexatriacontane (nC_{36}) standard.

2.1 Definitions

Analytical Batch - a set of one to twenty field samples of the same matrix and the associated quality control samples prepared on the same day and analyzed as a set.

Approximate Boiling Point/Carbon Number Distribution Marker Standard - a mixture of nC_6, nC_{12}, nC_{28} and nC_{35} n-alkanes used to determine the nC_6 to nC_{12}, $>nC_{12}$ to nC_{28}, and $>nC_{28}$ to nC_{35} boiling point ranges.

Alternate Approximate Boiling Point/Carbon Number Distribution Marker Standard - a mixture of nC_6, nC_8, nC_{10}, nC_{12}, nC_{16}, nC_{21} and nC_{35} n-alkanes used to determine the following boiling point ranges:

nC_6

$>nC_6$ to nC_8
$>nC_8$ to nC_{10}
$>nC_{10}$ to nC_{12}
$>nC_{12}$ to nC_{16}
$>nC_{16}$ to nC_{21}
$>nC_{21}$ to nC_{35}

Method Quantitation Limit (MQL) - as defined in Sections 7.4.1.2 and 7.5.1.1 of SW846-8000B.

Total Petroleum Hydrocarbon - for purposes of this procedure, total petroleum hydrocarbon is defined by the extraction procedure in this method and the area of all gas chromatographic peaks beginning with n-hexane ($n\text{-}C_6$) and ending with n-pentatriacontane ($n\text{-}C_{35}$). In some cases, the petroleum hydrocarbons in a sample may not be distributed through the entire range.

3.0 INTERFERENCE AND CONTAMINATION

Non-petroleum organic compounds which are soluble in n-pentane and which have boiling points in the range of interest can be measured under the conditions of this method; however, if present, the characteristic petroleum hydrocarbon pattern will be altered. When present, these non-petroleum organic compounds will be quantified as part of the TPH; therefore, the analyst must flag the data as presumptively containing significant amounts of non-petroleum compounds.

Contamination during sample preparation can be minimized by the use of disposable glassware. High purity reagent grade or pesticide grade n-pentane and methanol should be used to minimize contamination problems. A method blank should be analyzed with each analytical batch to demonstrate that the system is free from contamination. If samples are expected to have high concentrations it is also advised that instrument or solvent blanks be analyzed between GC runs to minimize contamination due to carryover or column/instrumental memory effects.

This method requires the use of a forced baseline. If drawn incorrectly, the resulting baseline will have a significant effect on the concentration reported. It is imperative that chromatograms be checked for correct baseline extension using a realistic scale relative to the chromatogram. Blanks and/or a low level standard should be analyzed to monitor for baseline drift.

4.0 APPARATUS AND MATERIALS

- Analytical balance (accurate to 0.0001 gram)

- Gas Chromatograph - Analytical system which includes a split/splitless injector, Electronic Pressure Control (EPC) (recommended), column supplies, gases, and syringes. A data system capable of storing and reintegrating chromatographic data and determining peak areas using a forced baseline, area summation, baseline projection, and performing baseline compensation is required.

- Autosampler - An autosampler capable of making 1-4 µL sample injections is strongly recommended to ensure consistent injection volumes and peak retention times.

- Flame Ionization Detector

- Recommended columns - 25/30 m x 0.25 mm fused silica capillary column with 0.25 µm to 1 µm film thickness (dimethylpolysiloxane or 5% phenylmethylpolysiloxane) or equivalent. Low bleed, high temperature, columns are preferred. Other capillary columns may be used if the elution of the compounds is based on boiling point and the required separation between the nC_5 peak and nC_6 peak is achieved. Capillary columns are required.

- Glassware -

  - 10 and 50 mL volumetric flasks.
  - 18 or greater gauge needles, i.e., the bore size should be no larger than an 18 gauge needle.
  - 20 mL glass scintillation vials with polytetrafluoroethylene (PTFE) lined screw-caps for dilution of oily wastes.
  - 3 and/or 10 mL glass vials with PTFE-lined screw-caps.
  - 5 and 10 mL glass, gas tight syringes.
  - 5 and 10 mL disposable serological pipets.
  - Disposable 2 mL Pasteur pipets.
  - Fine glass wool.
  - Pre-weighed (tared) 40 mL glass volatile organic analysis (VOA) vials with PTFE-faced silicon septa, label, and screw cap.

- Autosampler vials, 2 mL, with caps having PTFE-lined septa.

- Microsyringes - 10 µL to 1000 µL, glass, gas tight.

- Solid Extraction Mixer - vortex mixer; wrist action shaker; or horizontal shaker.

- Top-loading balance (accurate to 0.01 gram).

5.0 REAGENTS AND STANDARDS

5.1 Reagents

- Anhydrous Sodium Sulfate - Reagent grade, muffled at 425°C for 4 hours.

- Methanol - Capillary GC grade or equivalent, 99.9+% methanol, < 2 ng/L halogenated residue, < 1 ng/L organic residue, < 0.1% water, and < 0.0001% evaporation residue.

- n-Pentane - Capillary GC grade or equivalent, 98+% n-pentane, 99.9+% C_5 isomers, < 2 ng/L halogenated residue, < 1 ng/L organic residue, < 0.01% water, < 0.0001% evaporation

residue.

- Water - organic-free, reagent grade.
- Ottawa sand - muffled at 425°C for 4 hours if necessary to remove organic contamination.

5.2 Calibration and Stock Standard Solutions

Unless noted, standards are prepared in n-pentane and are stored at less than -12°C and kept no longer than a month. Standard preparation should follow the guidelines outlined in EPA SW846 Method 8000B. If available stock standards are purchased from commercial sources, the working standards must be in n-pentane.

- Petroleum Product Calibration Standard for Total Petroleum Hydrocarbons - Prepare a1% standard by accurately weighing approximately 0.05 to 0.1 g (recorded to the nearest 0.0001 g) of unleaded gasoline and diesel #2 in a 1:1 (either by volume or weight) ratio and diluting to volume with n-pentane in a 10 mL volumetric flask. Typical working concentration ranges are between 20 to 5000 µg/mL. Commercially available standards can be used as well.

- Approximate Boiling Point/Carbon Number Distribution Marker Stock Standard- Commercially available window defining hydrocarbon mixed standard containing approximately 200 µg/mL each of nC_6, nC_{12}, nC_{28}, and nC_{35}. This 1% standard may also be prepared by combining approximately 0.01 g (recorded to the nearest 0.0001 g) each of nC_6, nC_{12}, nC_{28}, and nC_{35} and diluting to volume with n-pentane in a 50 mL volumetric flask. Use an nC_{36} standard if an nC_{35} standard is not available.

- Alternate Approximate Boiling Point/Carbon Number Distribution Marker Stock Standard Commercially available window defining hydrocarbon mixed standard containing approximately 200 µg/mL each of nC_6, nC_8, nC_{10}, nC_{12}, nC_{16}, nC_{21}, and nC_{35}. (Use an nC_{36} standard if an nC_{35} standard is not available.) This alternate standard may also be prepared by combining approximately 0.01 gram (recorded to the nearest 0.0001 gram) each of the above n-alkane hydrocarbons and diluting to volume with n-pentane in a 50 mL volumetric flask.

  NOTE: The marker standards are used to determine the retention time windows for each boiling point range during the initial demonstration of proficiency procedures. The retention time windows should be checked during every run. When a shift greater than ±15 seconds is observed in the retention time for a boiling point range, the results for associated chromatograms should be recalculated.

- Surrogate Stock Solution - The analyst should monitor both the performance of the analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and water blank with surrogate compounds that encompass the range of the temperature program used in this method. Recommended surrogates are trifluoromethyl benzene or 1-chlorooctane for the nC_6 to nC_{12} range, and 1-chlorooctadecane, 2-fluorobiphenyl or o-terphenyl for the $>nC_{12}$ range. The surrogate stock solution can be

prepared by accurately weighing approximately 0.05 to 0.1 g (recorded to the nearest 0.0001 g) of a surrogate for each carbon range in a 1:1 (either by volume or weight) ratio and diluting to volume with n-pentane in a 10 mL volumetric flask.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Solid samples

- If solid samples are suspected to contain hydrocarbons in the nC_6 to nC_{12} boiling point range, refer to the website http://www.tnrcc.state.tx.us/permitting/trrp.htm for TNRCC guidance using Method SW846-5035 when collecting solid samples for volatile analysis and implement the following modification: The size of the sample for TNRCC Method 1005 analysis that is collected should be approximately 10 g and the sample should be collected using a coring device, extruded into a tared 40-mL VOA vial with a PTFE-lined septum cap, and hermetically sealed in the field. The laboratory should extract the solid sample according to the procedures herein. Unused and unopened samples collected, preserved, and held in this manner can also be used for some solid volatile analyses, such as BTEX by SW846-8260 or SW846-8021 provided the sample size of 10 g is appropriate.

- If hydrocarbons within the nC_6 to nC_{12} boiling point/carbon range are not suspected based on existing analytical data such as SW846-8021 data, refer to SW846, Chapter Four, Organic Analysis, Section 4.1 for collecting solid samples for semi-volatile analysis. Unused samples collected in this manner can also be used for some semi-volatile or non-volatile analyses, such as SW846-8270 or SW846-8082.

- The holding time for solid samples is 14 days from collection to extraction and 14 days from extraction to analysis. Prior to extraction, the sample should be held at or below -12EC until extraction. Once extracted, the extract should be tightly capped and stored at or below -12EC until the time analysis.

6.2 Aqueous samples

Refer to SW846, Chapter Four, Organic Analysis, Section 4.1 for collecting aqueous samples for volatile analysis. Prior to the n-pentane extraction, unopened and unused samples collected, preserved, and held in this manner can be used for some aqueous volatile analysis, such as BTEX by SW846-8021 or SW846-8260.

Aqueous samples should be preserved to a pH of less than 2 with sodium bisulfate, hydrochloric acid, or sulfuric acid. The type of preservative and resultant pH should be documented on the field chain of custody documentation.

If the aqueous sample is preserved to a pH of less than 2, the holding time is 14 days from collection to extraction and 14 days from extraction to analysis. If the aqueous sample is not preserved, the holding time is 7 days from collection to extraction and 14 days from extraction to

analysis. Prior to extraction, the sample should held at or below 4 ±2EC. Once extracted, the extract should be tightly capped and stored at or below -12EC until the time analysis.

7.0 PROCEDURE

7.1 Sample Preparation

Prior to analysis, all samples must be extracted with n-pentane. Pressure differences that may develop in a vial during the preparation procedures can be equilibrated using a second needle pierced through the septum while the sample is being taken from the vial using a glass, gas-tight syringe. When n-pentane is being added to the vial and before using a second needle to equilibrate the pressure, enough n-pentane should be added to the vial and mixed in such a way as to capture into the n-pentane any hydrocarbons that may have volatilized into the head space.

All syringes used must be glass, gas-tight syringes. All needles used during the preparation of the sample(s) should have bore sizes smaller than or equal to an 18 gauge needle.

7.1.1 Solid extraction

- For samples collected in VOA vials, remove the sample vial from refrigeration and allow it to reach room temperature. Dry the outside of the vial. Weigh each vial and its contents on a top loading balance and record the weight to the nearest 0.01 g. Subtract the tare weight of the VOA vial. Record the resulting sample weight.

- For samples collected in conventional glass jars (bulk samples), remove the sample container from refrigeration and allow it to reach room temperature. Using the laboratory's SOP for subsampling a solid matrix for extractable hydrocarbons, transfer 10 ±0.01g of sample into a VOA vial with a PTFE-lined septum cap. Record the weight of the sample.

- Prepare quality control samples.

  - <u>Method blank and laboratory control sample (LCS) and laboratory control sample duplicate (LCSD)</u>: Prepare by weighing 10 g ±0.01 g of Ottawa sand, or other blank standard solid, into a VOA vial with a PTFE-lined septum cap.

  - <u>Matrix Spike/Matrix Spike Duplicate (MS/MSD)</u>: For solid MS/MSD, use an appropriate environmental sample, i.e., use the replicate field samples that were collected using SW846-5035 techniques, or weigh 10 g ±0.01 g of the environmental bulk sample into a 40-mL vial with a PTFE-lined septum cap.

  - Transfer 250 FL of Petroleum Product Calibration standard into the LCS, LCSD, MS and MSD samples using a gas-tight glass syringe. Mix by vortexing or hand shaking 1 minute.

- Transfer 250 FL of the Surrogate Stock Solution into all samples, including environmental samples, LCS, LCSD, MS, and MSD samples using a gas-tight glass syringe. Mix by vortexing or hand shaking 1 minute.

- Add 10 mL of n-pentane to all samples through the septa of the vials using a 10-mL gas-tight glass syringe and vortex or shake by hand at least 1 minute. Let particulate material settle a minimum of 1 hour but can take as long as overnight.

  NOTE: Solids heavily laden with hydrocarbons must be extracted 3 times with 10 mL of n-pentane, transferring the extract each time to a 50 mL graduated cylinder with a ground glass stopper. Measure and record the extract volume on the extraction worksheet.

  NOTE: If particulate is suspended in the solvent layer or an emulsion forms, centrifuge the extract to obtain a clear solvent layer.

- Uncap the VOA vial and transfer 1-2 mL of the sample extract to an autosampler vial using a Pasteur pipet. Cap the autosampler vial with a PTFE-lined cap.

  NOTE: If methanol was added to the sample to aid in breaking up the clay, add 3-4 mL of reagent water and swirl gently to remove excess dissolved methanol from the extraction solvent and to clearly define the boundary between the pentane and methanol/water mixture.

  NOTE: If the extract is to be stored, store the tightly capped vial at or below -12EC.

7.1.2 Aqueous Extraction

- Remove the sample vial(s) from refrigeration and allow it to reach room temperature.

- Prepare aqueous quality control samples.

- From all samples, i.e., environmental and quality control samples, remove approximately 10 mL of the sample through the septum with a syringe. It is recommended that an additional needle be inserted into the septum to allow for the equalization of pressure as the 10 mL is withdrawn from the vial. Discard the 10 mL. Dry the outside of the vial. Weigh the vial and its contents on a top loading balance and record the weight to the nearest 0.01 g. Subtract the tare weight of the VOA vial. Record the resulting sample weight.

- Inject 100 FL of Petroleum Product Calibration standard through the septa into the LCS, LCSD, MS, and MSD. Mix by hand shaking 1 minute.

- Inject 100 FL of the Surrogate Stock Solution through the septa into all samples, including environmental samples, LCS, LCSD, MS, and MSD samples using a gas-tight glass syringe. Mix by vortexing or hand shaking 1 minute.
- Into all samples, inject 3 mL of n-pentane through the septum using a 5-mL syringe.
- Extract by vigorously vortexing for at least 2 minutes.
- Uncap the vial and fill a 2-mL autosampler vial, using a Pasteur pipet. Cap the autosampler vial with a PTFE-lined cap.

NOTE: If the extract is to be stored, store the tightly capped vial at or below -12EC.

7.1.3 Petroleum Samples

If a sample of neat petroleum product, crude oil, or waste is to be analyzed, the sample should be diluted with n-pentane (1:500 to 1:1000) and analyzed directly.

7.2 GC Chromatography

7.2.1 Gas Chromatographic Conditions

The GC conditions listed in this method are recommended. Changes to the method chromatographic conditions can be made by the analyst in order to improve the speed of analysis, lower the cost of analysis, and/or improve the separation or lower the detection limit as long as the changes are documented in the laboratory's SOP for this method, and the changes meet the initial and continuing calibration criteria and quality assurance criteria listed in this method, and allows the analyst to achieve the required separation between the nC_5 and the nC_6 peaks.

Oven program: Typical run time is 30 minutes, but may be more or less depending on the column and the GC conditions used by the laboratory to achieve the required separation between the nC_5 and nC_6 peaks. Set the initial column oven temperature to 30°C. Hold this temperature for 3 minutes. Increase the temperature by 15°C/minute until reaching 300°C. Hold this temperature for 5 minutes. Increase the oven temperature by 15°C/minute until reaching 325°C. Hold this temperature for the remainder of the run. An equivalent program can be run provided data are generated that document the quality control criteria of the method are met.

Sample/autosampler injection: 1.0 to 1.5 FL splitless injection. Septum purge flow 15 seconds after injection at 20 mL/minute.

Carrier gas: Helium at 3.0 mL/minute for 26.0 minutes and at 6.0 mL/minute for the final four minutes of the run.

Make-up gas: Helium

FID hydrogen: Approximately 40 mL/minute

FID air: Approximately 450 mL/minute

FID temperature: 325°C.

Injector temperature: 285°C.

7.2.2 Retention Time Windows

Retention time windows are established during the method setup and checked every run by analyzing the appropriate mix of marker standards after the method blank analysis. An evaluation should be performed to ensure that the response factor for the nC_{35} peak is greater than or equal to 75% of the response factor of the nC_{28} peak. If the response factor for nC_{35} is less than 75 percent of the response factor for nC_{28}, the problem(s) must be corrected and the retention time windows re-established for each boiling point range.

For a given range (e.g., $>nC_{12}$ to nC_{28}), the retention time (RT) window is defined as beginning 0.1 minutes after the RT of the first marker compound (e.g., nC_{12}) and ending 0.1 minutes after the RT of the ending marker compound (e.g., nC_{28}). If performed properly for the example range, i.e., $>nC_{12}$ to nC_{28}, the nC_{12} is not included in the reported result and the nC_{28} is included in the reported result.

A default window of ± 0.1 minute is acceptable for this method because capillary columns have sufficient overall long term stability to maintain retention time properly. The retention time window should be reassessed for each standard on each GC column during every analytical batch and whenever a new GC column is installed.

7.3 Calibration

7.3.1 Initial calibration

- Using n-pentane, prepare a minimum of five calibration standards from the Petroleum Product Calibration Standard ranging in concentration from 20 to 1000 mg/L.

- Inject each standard into the gas chromatograph using the same conditions, e.g., injection volume and technique, to be used during sample analysis.

- Tabulate peak area responses against the concentration injected using peak to valley integration for the nC_6 to nC_{12} range and a forced baseline projection for the $>nC_{12}$ to nC_{28} range, or when applicable to nC_{35}.

  NOTE: When using forced baseline projection, it is preferable to initiate the baseline projection at some point prior to elution of the solvent peak.

- If a linear regression analysis is performed, the correlation coefficient must be $\geq$ 0.995. If the average response factors or average concentration factors are calculated, the percent relative standard deviation (RSD) must be ±25% over the working range.

7.3.2 Calibration Verification

Before analysis can begin, the working calibration factor or calibration curve must be verified using the following procedures:

- Analyze a mid-point calibration standard at the beginning of each working day on which TPH analysis will occur and at the end of each batch of 20 samples, each shift, or each work day, whichever is more frequent.

- Calculate the relative percent difference. Recalibrate the instrument if the relative percent difference is > ± 25%. Reanalyze all sample analyzed after the last acceptable check standard.

- It is advisable to check instrument performance further by the analysis of a low concentration standard.

7.4 Sample Analysis

The analyses of all samples, including field samples, spike samples, laboratory control samples, method blanks, and other quality control samples, are performed during an analysis sequence, e.g., initial calibration, calibration verification, method blank, laboratory control sample, spiked samples and duplicates, environmental samples, instrument blank, and calibration verification. The sequence ends when the calibration verification sample has been successfully analyzed or when quality control criteria have not been met. Sample concentrations are calculated by comparing sample responses with the initial calibration of the system.

For samples containing unresolved hydrocarbons, use a forced baseline to generate the area for TPH calculation or for a group of hydrocarbons within a defined carbon range. No chromatographic areas related to unresolved hydrocarbons may be disregarded in determining TPH concentration.

If the product concentration exceeds the linear range of the method (i.e., highest standard in the calibration curve) in the final extract, dilute and reanalyze the extract.

7.5 Calculations

Unless specified otherwise by the data user or the project objectives, a percent moisture determination should be performed and the results reported with the dry weight results.

7.5.1 TPH Concentration (Solid)

$$C_s = (C_c \times V_t \times D) / W_s$$

Where,

C_s	=	Concentration of TPH in sample in mg/kg.
C_c	=	Concentration of TPH in extract in mg/L.
V_t	=	Volume of final extract in L.

D	=	Dilution/concentration factor.
W_s	=	Weight of sample in kg.

NOTE: If the sample is presumed to have more than 5% by volume as TPH, the extract volume must be measured (< 5% error) and recorded in order to correct for the increase in extract volume due to the extraction of the petroleum hydrocarbons into the n-pentane.

7.5.2 TPH Concentration (aqueous)

$$C_s = (C_c \times V_t \times D)/W_s$$

Where,	C_s	=	Concentration of TPH in sample in mg/L.
	C_c	=	Concentration of TPH in extract in mg/L.
	V_t	=	Volume of final extract in L.
	D	=	Dilution/concentration factor.
	W_s	=	Volume of sample extracted in L.

7.5.3 Calibration Factor

$$CF = A/C$$

Where,	CF	=	Calibration factor.
	A	=	Total area of calibration standard.
	C	=	Concentration of calibration standard in mg/L.

7.5.4 Percent Relative Standard Deviation

$$\%RSD = (S/\bar{x}) \times 100$$

Where,	%RSD	=	Percent Relative Standard Deviation.
	S	=	Standard deviation of the 5 calibration factors.
	$\bar{x}$	=	Mean of a minimum of 5 calibration factors.

7.5.5 Percent Difference

$$\%D = (CF_x - CF_v)/CF_x \times 100$$

Where,	%D	=	Percent difference.
	CF_x	=	Average calibration factor.
	CF_v	=	Calibration factor of verification standard.

7.5.6 Percent Recovery (LCS and MS, MSD)

$$\%R_{LCS} = (X_m/X_t) \times 100 \qquad \%R_M = [(SSR - SR) / SA] \times 100$$

Where,	$\%R_{LCS}$	=	Percent recovery LCS.	Where	$\%R_M$	=	Percent Recovery MS/MSD
	X_m	=	Measured value.		SSR	=	Spiked sample result.
	X_t	=	True value.		SR	=	Sample result,
					SA	=	Spike added.

7.5.7 Relative Percent Difference

$$RPD = [(X_1 - X_2)/((X_1 + X_2) / 2)] \times 100$$

Where, RPD = Relative percent difference.
X_1 = First measured value.
X_2 = Second measured value.

8.0 QUALITY CONTROL

The laboratory should maintain a formal and documented quality control program generally consistent with the NELAC standards and should maintain records to document the quality of data generated.

The quality control procedures necessary to evaluate the GC system operation are found in SW846-8000B. Check the performance of the entire analytical system daily using data gathered from analyses of blanks, standards, and replicate samples. If any of the chromatographic QC limits are not met, the analyst should examine the GC system to determine the cause. If the cause of the problem requires shutting down of the GC system, a calibration verification standard should be reanalyzed before any samples are analyzed.

8.1 Method Detection Limit

Prior to analyzing samples, the laboratory must determine the method detection limit (MDL) for each instrument used. The guidelines specified in SW-846 or 40 CFR, Part 136, Appendix B should be used to determine the MDL, and as specified in 40 CFR, Part 136, Appendix B. In general, the MDL should be reported no lower than a value 3 to 5 times below the concentration of the lowest non-zero standard.

8.2 Initial Demonstration of Capability

Each laboratory performing TPH analysis must demonstrate the capability to perform assigned components of TPH analysis and meet the acceptance criteria stated below.

For a solid matrix, extract and analyze a minimum of 4 Ottawa sand blanks (10 grams each) spiked with 250 µL of the TPH working calibration standard containing the lowest concentration.

For an aqueous matrix, extract and analyze a minimum of 4 reagent aqueous blanks spiked with 100 µL of a TPH working calibration standard containing the lowest concentration.

Calculate the following:

- TPH of each sample for carbon range C_6 to C_{35};
- Average percent recovery; and
- Relative standard deviation.

Average Percent recovery should be between 75% and 125%. Relative standard deviation should be ±20% or less.

Repeat the initial demonstration of capability if:

- A change is made in instrument type, personnel, or matrix;
- A laboratory or analyst is unable to meet acceptance criteria for the demonstration of capability;
- A new analyst(s) is trained on this method; or
- Quality systems, method-related, or operational problems having the potential to affect data quality are suspected or confirmed.

8.3 Performance Evaluation Sample

Successfully analyze available performance evaluation samples from an independent commercial source for both solid and aqueous samples at both low (5-10 mg/L for aqueous and 50-100 mg/kg for solid) and high (20-100 mg/L for aqueous and 1,000-20,000 mg/kg for solid) concentrations. Data and chromatograms for these samples must be kept on file at the laboratory. Analyze performance evaluation samples annually.

8.4 Instrument Quality Control

The n-hexane (nC_6) peak must be adequately resolved (capable of being integrated as an independent peak) from the n-pentane (nC5) solvent in the chromatographic run.

Retention time windows must be established for n-hexane (C_6), n-dodecane (C_{12}), n-octacosane (C_{28}) and n-pentatricontane (C_{35}), or for each carbon marker in the alternate carbon locator mix, each time a new GC column is installed and must be verified and/or adjusted on a daily basis.

Calibration curves must be developed based upon the analysis of calibration standards prepared at a minimum of 5 concentration levels. The linearity of calibration or response factors may be assumed if the percent relative standard deviation (%RSD) over the working range of the curve is less than or equal to 25%. Alternatively, if linear regression analysis is used for quantitation, the correlation coefficient (r) must be at least 0.995. Each laboratory must generate control limits based on the average recovery ± 3 standard deviations as determined from the results of the laboratory control sample. These control limits must be within 75% to 125% recovery and should be statistically generated and used to control the analytical system.

A summary of quality control checks, the minimum frequency at which those checks should be performed, the acceptance criteria those checks should meet, and the corrective action(s) that should be taken if the acceptance criteria are not met are presented in Table 8-1. All data associated with quality control checks not meeting the acceptance criteria should be flagged by the laboratory to advise the data user.

Table 8-1: Summary of Calibration and QC Procedures for TNRCC Method 1005

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action*
Minimum five-point initial calibration.	Initial calibration prior to sample analysis.	Mean RSD for TPH #25% or correlation coefficient for linear regression $0.995.	Correct problem then repeat initial calibration.
Calibration verification.	At the beginning of each working day on which TPH analysis will occur and at the end of each batch of 20 samples , each shift, or each work day, whichever is more frequent.	RPD #25% of expected value.	Correct problem then repeat initial calibration.
Demonstrate ability to generate acceptable accuracy and precision using four replicate analyses of a QC check sample.	Initially prior to analysis of any samples and in response to changes in staff, instrumentation, or operations.	Average %R within 75-125% and RSD #20% or within laboratory limits.	Recalculate results; locate and correct problem with system and then rerun demonstration for those analytes that did not meet criteria.
Method blank.	One per analytical batch of 20 samples or less.	No TPH detected $ MQL.	Correct problem then reprep and analyze method blank and all samples processed with the contaminated blank.
LCS and LCSD.	One LCS/LCSD per analytical batch of 20 samples or less.	%R within 75 - 125% and RPD ± 20% or within laboratory limits.	Correct problem then reprep and analyze the LCS and all samples in the affected analytical batch.
MS/MSD.	One MS/MSD per every 20 project samples per matrix.	%R within 75 - 125% and RPD ± 20% or within laboratory limits.	None.
Retention time window check.	Once per analytical batch of 20 samples or less.	The RF for nC_{35} is $\geq$ 75% the RF for nC_{28}.	Correct problem then reestablish the RT windows and reanalyze all samples analyzed since the last retention time checked.
Surrogate Recoveries	Spiked into every sample including all QC samples.	%R within 70 - 130% or laboratory established limits.	Reanalyze, or reextract and reanalyze, or flag the data.
Performance Evaluation samples	Once per 12 month period.	within manufacturer's statistical guidelines.	Reextract/reanalyzed. If still out, correct problem and reanalyze.
MDL study.	Once per 12 month period.	Detection limits established shall be # ½ the MQLs .	None.

* All corrective actions associated with project work should be documented, and all records should be maintained by the laboratory.

9.0 DATA REPORTING

The quantified results of the analysis should be reported as specified by the data user or the project objectives. The calculated concentration of TPH should be reported for each boiling point range specified by the project objectives. If heavier hydrocarbons are not present in the sample, the analysis and the reported results can be truncated at the nC_{28} marker.

9.1 Analytical Report

Unless other reporting requirements are specified in work orders, project plans, or other documents, include at a minimum the following information in analytical reports:

- Client name and sample identification number;
- Laboratory name and sample identification number;
- Sample matrix (e.g., solid, sediment, sludge, aqueous);
- Type of sample received, i.e., closed system vial or bulk jar sample;
- Sample collection and laboratory receipt dates;
- Sample extraction and analysis dates;
- Calculated dry weight concentration of TPH for carbon ranges specified by the data user or project objective, such as nC_6 to nC_{12}, $>nC_{12}$ to nC_{28}, $>nC_{28}$ to $nC_{35,}$ and either nC_6 to nC_{28} or nC_6 to nC_{35};
- Percent moisture or percent solids result for solid samples, if requested or specified;
- Method blank, spike and spike duplicate recoveries, and laboratory control sample recoveries and RPDs;
- Case narrative or laboratory review checklist documenting laboratory's review of the data; and
- Chromatograms, data tables, and interpretations, if requested

10.0 HEALTH AND SAFETY, POLLUTION PREVENTION, WASTE MANAGEMENT

The toxicity of chemicals used in this method has not been precisely defined. However, each chemical should be treated as a potential health hazard. The laboratory is responsible for maintaining a current awareness file of Occupational Safety and Health Administration (OSHA) regulations regarding safe handling of chemicals specified in the method. A reference file or material safety data sheets (MSDS) should be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety should be available and should be identified for use to the analyst.

The solvents used in this method pose little threat to the environment when recycled and managed properly. The quantity of chemicals purchased should be based on the expected usage. Standards should be prepared in volumes so as to minimize the amount of waste disposed.

Samples and extracts should be retained or disposed of in accordance with instructions from the client. It is the laboratory's responsibility to comply with all federal, state, and local requirements governing waste management, particularly those concerning hazardous waste identification and disposal, and to protect the air, water, and land by minimizing and controlling releases from fume hoods and bench operations.

Unless otherwise specified and required, records produced by this method should be maintained a minimum of seven years following the end of the year in which they were produced.

11.0 REFERENCES

Tong, H.Y., Karasek, F.W., "Flame Ionization Detector Response Factors for Compound Classes in Quantitative Analysis of Complex Organic Mixtures", Analytical Chemistry, 56, 2124-2128, 1984.

API Publication Number 4599: "Interlaboratory Study of Three Methods for Analyzing Petroleum Hydrocarbons in Solids: Diesel-Range Organics (DRO), Gasoline-Range Organics (GRO), Petroleum Hydrocarbons (PHC)", June 1994.

USEPA Test Method for the Evaluation of Solid Waste (SW-846), 3rd Edition, update III.

Rhodes, I.A.L., Olvera, R.Z., Leon, J.L., Hinojosa, E.M., "Determination of Total Petroleum Hydrocarbons by Capillary Gas Chromatography", Proceedings of the Fourteenth Annual EPA Conference on Analysis of Pollutants in the Environment", Norfolk, VA, 1991.

Rhodes, I.A.L, Hinojosa, E.M., Barker D.A., Poole, R.L, "Pitfalls Using Conventional TPH Methods for Source Identification: A Case Study", Proceedings of the Seventeenth Annual EPA Conference on Analysis of Pollutants in the Environment", Norfolk, VA, 1994.

Rhodes, I.A.L, Hinojosa, E.M., Barker D.A., Poole, R.L, "Conventional TPH Pitfalls", Environmental Lab, December/January 1995/96.

ASTM Method D 4547-91, "Standard Practice for Sampling Waste and Solids for Volatile Organics", 1991.

40 CFR Part 136, Appendix B.

"Total, Fixed, and Volatile Solids in Solid and Semisolid Samples," Standard Methods for the Examination of Water and Wastewater, 18th Edition (1992), p 2-58.

EPA Method 5035, "Closed-System Purge -and-Trap and Extraction for Volatile Organics in Solid and Waste Samples," Revision 0, December 1996, SW 846 Final Update III, December, 1996, U.S. Environmental Protection Agency.

12.0 QUESTIONS AND COMMENTS

Questions and comments may be mailed to:

Method 1005
Texas Natural Resource Conservation Commission
P.O. Box 13087, MC-176
Austin, TX 78711-3087

Electronic mail concerning Method 1005 may be sent to: techsup@tnrcc.state.tx.us.

APPENDIX 1
SUPPLEMENTAL INFORMATION

BOILING POINTS

Petroleum hydrocarbons in the nC_6 to nC_{28} range boil between approximately 65°C to 450°C. This range includes gasoline, kerosene, number 2 diesel fuel, some light lubricating oils, and some portions of other, heavier fuel and lubricating oils.

REAGENTS

Capillary GC grade n-pentane and methanol should be used to minimize contamination problems. Most grades of n-pentane contain some n-hexane and the concentration of the n-hexane varies from manufacturer to manufacturer and even from lot to lot from the same manufacturer. This has caused some concern among some analysts. All reagents should be checked for contamination prior to use. The amount of n-hexane should be determined. If the concentration of n-hexane found is above the reporting limit of interest, then a different grade, lot number, or manufacturer of n-pentane should be used. However, if all sources of n-pentane contain some n-hexane, an n-pentane from the same manufacturer, grade, and lot number should be used to make up the standards and used for the sample extraction. This procedure will ensure that the contribution of the n-hexane will be negligible because the concentration will offset the calibration curve, increasing the value of the y-intercept. Any increases in sample volume during the extraction, which will lower the relative concentration of the n-hexane, will minimally impact the result.

Methanol, which is used in the extraction of solid samples, has been reported to chromatograph as a "hump" with a shallow slope in the gasoline range. This could cause baseline problems in the integration of the samples resulting in poor QC. Using a forced baseline in this region, the "hump" is always integrated and gives a substantial false positive result. This problem can be reduced by either: 1) Adding several mL of water to the extraction vial and allowing extra time for the dissolved methanol to partition into the water, or 2) by saturating the n-pentane used for extractions and to make standards with methanol, and using baseline projection and area summation, which will offset the calibration curve by matching the solvent matrix.