Draft TNRCC METHOD 1006

Characterization of Nc_6 to Nc_{35} Petroleum Hydrocarbons in Environmental Samples:

- **ALIPHATIC HYDROCARBONS**
- **AROMATIC HYDROCARBONS**
- **APPROXIMATE BOILING POINT/CARBON NUMBER DISTRIBUTION**

1.0 SCOPE AND APPLICATIONS

- This method is in draft form and can be used by the laboratory provide adequate quality control data are generated and are within the acceptance criteria specified in the method.

- This method is designed to separate and quantify the aliphatic and aromatic fractions in petroleum hydrocarbons extracted soil and water samples. The separation is based on approximate carbon number/boiling ranges with respect to n-alkane markers from n-hexane (nC_6) to n-pentatriacontane (nC_{35}). The method is applicable to hydrocarbons in the gasoline and diesel ranges and portions of the heavier fuel and lubricating oil range. This method is to be used in conjunction with TNRCC Method 1005 which is used for the determination of total petroleum hydrocarbons (See Figure 1).

- This method is not intended for the quantitation of individual target analytes, such as BTEX and PAHs. Those target analytes are best determined using EPA Methods 8021, 8260 or 8270, where appropriate. However, an estimate of the concentrations of individual target analytes may be obtained using this method.

- Gas chromatography (GC) is used for separation with flame ionization (FID) as the mode of detection. The response of the FID is generally equal for all hydrocarbons on a weight and effective carbon number basis. The method reporting limit for TPH using TNRCC Method 1005 is estimated to be 50 mg/kg in soil and 5 mg/L in water depending on the number of hydrocarbon components present in the nC_6 to nC_{35} range. For this method, the soil reporting limits for each fraction range can be reported down to 10 mg/kg for soil samples and 1 mg/L for water samples. Lower reporting limits are possible depending on the distribution of hydrocarbons in each range.

- This method should be used by, or under the supervision of, analysts experienced in the use of solvent extraction, solid phase fractionation 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 use of peak processing software with baseline and peak grouping functions.

- The extraction and fractionation procedure can take as little as 15 minutes to perform per sample. GC analyses may take 20 to less than 90 minutes depending on the

chromatographic column used and the GC parameters. Three separate GC analyses per sample are required to obtain data for the total petroleum hydrocarbons (as specified in TNRCC Method 1005), data for the total aliphatic fraction, and data for the total aromatic fraction. It is strongly recommended that the sample extract be analyzed first by TNRCC Method 1005 to determine the type of petroleum hydrocarbons (if any) present in the sample and to review the project objectives before proceeding with the fractionation step (See Figure 1). Additionally, data from TNRCC Method 1005 can be used for potential product source identification, to assess if there are different types or distributions of petroleum hydrocarbons in a sample, or to determine if fractionation is necessary.

- TNRCC Methods 1005 should be used for the purposes of determining concentrations of TPH for evaluating risk and/or determining the composition of TPH. TNRCC Method 1006 can be used on selected samples to determine the mass of TPH within defined boiling point ranges in the aliphatic and aromatic fractions of the TPH.

- TNRCC Method 1005 is an n-pentane extraction followed by gas chromatography/flame ionization detection (GC/FID) analysis method that measures the concentration of hydrocarbons between nC_6 and nC_{35}. The laboratory includes a nC_{12} alkane marker and a nC_{35} alkane marker to aid the data user in evaluating the distribution of the hydrocarbons in the TPH based on the chromatographic profile. The analytical results from TNRCC Method 1005 are used to measure the concentration of TPH in the affected environmental media and to evaluate the relative distribution of the petroleum hydrocarbons in the total mixture.

- TNRCC Method 1006 uses a silica gel column fractionation of the n-pentane extract (obtained using TNRCC Method 1005) to separate the TPH into the aliphatic hydrocarbon fraction and the aromatic hydrocarbon fraction and includes the analysis of each of these fractions by GC/FID. Quantitation is done using the TNRCC Method 1005 calibration extended to nC_{35}. The GC/FID analysis of the fractions separates each fraction into discrete boiling point ranges based on normal alkane markers. The boiling point ranges for each fraction are presented in Table 1. The concentration within each boiling point range (e.g., $>nC_8$ - nC_{10} aliphatic or $>nC_{12}$ - nC_{16} aromatic) is reported along with the total TPH concentration between nC_6 and nC_{35}.

2.0 SUMMARY OF METHOD

TNRCC Method 1005 involves extraction of a soil or a water sample with n-pentane and analysis of a portion of the extract using gas chromatography with a flame ionization detector (GC-FID). TNRCC Method 1006 is an extension of TNRCC Method 1005 for additional characterization of petroleum hydrocarbons. The fractionation of the petroleum hydrocarbon extract is accomplished by solid phase column separation of a portion of the n-pentane extract using silica (similar to EPA Method 3630) and eluting the column with additional n-pentane to obtain an aliphatic fraction followed by elution with dichloromethane to obtain an aromatic fraction. The fractions are analyzed using GC-FID as specified in TNRCC Method 1005. The

aliphatic and aromatic fractions are further characterized by subdividing the chromatographic data into approximate boiling point/carbon number ranges listed in Table 1 with respect to n-alkane.

Table 1: Approximate Boiling Point/Carbon Number Ranges for TNRCC Method 1006.

Aliphatics	Aromatics
nC_6	
$>nC_6$ to nC_8	$>nC_7$ to nC_8 (Toluene only)
$>nC_8$ to nC_{10}	$>nC_8$ to nC_{10}
$>nC_{10}$ to nC_{12}	$>nC_{10}$ to nC_{12}
$>nC_{12}$ to nC_{16}	$>nC_{12}$ to nC_{16}
$>nC_{16}$ to nC_{21}	$>nC_{16}$ to nC_{21}
$>nC_{21}$ to nC_{35}	$>nC_{21}$ to nC_{35}

This method uses the same calibration curve as TNRCC Method 1005 that uses a 1:1 mixture of gasoline and diesel for calibration. However, either a mixture of petroleum products (such as gasoline or diesel) or single hydrocarbon components can be used for calibration. The choice of calibration standards should be the same for both methods. Currently, TNRCC Method 1005 calibration is based on a mixture of gasoline and diesel.

3.0 DEFINITIONS

Total Petroleum Hydrocarbons (TPH) are defined in TNRCC Method 1005 as all gas chromatographic peaks detected using flame ionization detection eluting after the solvent (n-pentane) starting with and including n-hexane(nC_6) to n-pentatriacontane (nC_{35}). This definition includes aliphatic and aromatic hydrocarbons. The petroleum hydrocarbons in a sample (if any) may not be distributed throughout the entire range. This information is useful for product or source identification. There may be non-hydrocarbon compounds that elute in this range (such as chlorinated solvents, ketone, alcohols, etc.). However, such compounds usually appear as discrete peaks and do not match typical petroleum product fingerprints.

Aliphatic Hydrocarbons are defined in this method as those compounds detected from n-hexane (nC_6) to n-pentatriacontane (nC_{35}) (inclusive) in the chromatogram of the aliphatic fraction.

Aromatic Hydrocarbons are defined in this method as those compounds detected from n-heptane (nC_7) to the retention time of n-pentatriacontane (nC_{35}) in the chromatogram of the aromatic fraction. The first aromatic compound in this range is toluene. However, this method is recommended to detect aromatics starting with the C_8 to C_{10} range. Benzene and toluene (nC_6 to nC_8 range) should be measured using EPA Methods 8260 or 8021 which are more selective to these compounds and have lower detection limits. If ethylbenzene and xylenes are required to be specifically identified and to be quantitated as individual components, then they should also be determined using EPA Methods 8260 or 8021.

Approximate Boiling Point/Carbon Number Distribution is defined as the subdivision of the chromatogram into sections that correspond to the approximate boiling point and/or volatility of n-alkanes. The gas chromatographic separation is achieved using a column that separates components based primarily on boiling point differences. This separation can be correlated to approximate carbon number. For example, >nC_7 to nC_8 indicates those hydrocarbons that elute after n-heptane and up to and including n-octane. This range includes most, but not all, of the C_8 hydrocarbons. Branching lowers the boiling points of hydrocarbons relative to their n-alkane isomers. Cyclization, or ring structures, raises the boiling point higher than the n-alkanes of the same carbon number. Thus, there are some C_8 hydrocarbons that elute before n-heptane and there are some that elute after n-octane, including the aromatics ethylbenzene and the xylenes. Table 2 lists the approximate boiling point ranges for the n-alkanes.

This method allows for data reporting between each carbon range or for reporting within wider carbon ranges depending on data quality objectives.

Table 2: Boiling points of n-alkanes used for the determination of approximate boiling point/carbon number distribution. Retention times based on GC conditions described in this method must be determined experimentally**. Minimum required markers that defined the ranges of interest are shown in bold and shaded.**

n-Alkane Marker	Boiling Point, ˚C	n-Alkane Marker	Boiling Point, ˚C
nC_6	69	**nC_{21}**	357
nC_7	98	nC_{22}	369
nC_8	126	nC_{23}	380
nC_9	151	nC_{24}	391
nC_{10}	174	nC_{25}	402
nC_{11}	196	nC_{26}	412
nC_{12}	216	nC_{27}	422
nC_{13}	236	**nC_{28}**	431
nC_{14}	253	nC_{29}	441
nC_{15}	270	nC_{30}	450
nC_{16}	287	nC_{31}	458
nC_{17}	302	nC_{32}	467
nC_{18}	316	nC_{33}	474
nC_{19}	329	nC_{34}	481
nC_{20}	343	**nC_{35}**	499

4.0 INTERFERENCES

Other organic compounds which are soluble in n-pentane and are not retained by silica and that have boiling points in the range of interest could be measured under the conditions of this method. However, if present, the characteristic petroleum hydrocarbon patterns will be altered. These compounds will be quantified as part of the TPH, but the data must be flagged as presumptively containing significant amount of such compounds. The aliphatic and aromatic fractions obtained by this method are less susceptible than the TPH obtained using TNRCC Method 1005 to interferences from some types of materials because the fractionation process may remove the interference.

Sample contamination due to sample preparation may be minimized by the use of disposable glassware. High purity reagent grade or pesticide grade n-pentane, acetone and dichloromethane should also 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 solvent blanks be analyzed between GC runs to minimize contamination due to carryover.

This method depends on correctly integrating a mass of unresolved peaks, usually found in the approximate nC_{10}-nC_{35} range, using a forced baseline. The resulting baseline, if drawn incorrectly, will have a significant effect on the concentration reported. It is imperative that chromatograms be checked (using a realistic scale relative to the chromatogram) for correct baseline extension. Blanks and/or a low level standard should be run to monitor for baseline drift. Peaks in the approximate nC_6-nC_{12} range are normally discrete and can be integrated valley to valley.

5.0 LABORATORY EQUIPMENT AND SUPPLIES

As specified in TNRCC Method 1005

- Additional Glassware:
  - 1 cm I.D. by 10 to 20 cm glass column with glass or Teflon stopcock.
  - Kuderna-Danish concentrator tube or equivalent vials

- Gas Chromatograph:

  As specified in TNRCC Method 1005

6.0 REAGENTS AND STANDARDS

6.1 Reagents

- n-Pentane, dichloromethane, acetone, methanol: Pesticide grade or equivalent, <1 mg residue.

- Sodium Sulfate: Granular, anhydrous, reagent grade muffled at 425 ^{o}C for 4 hours.

- Organic Free Reagent Water.

- Silica gel, 100/200 mesh desiccant. Before use, activate for at least 16 hours at 130°C in a shallow glass tray, loosely covered with foil.

- Alumina - Neutral (5% Deactivated)

6.2 Calibration & Stock Standard Solutions

Unless noted, standards are prepared in n-pentane and are stored at -15°C. Standard preparation should follow the guidelines outlined in EPA SW-846 Method 8000B. If available stock standards are purchased from commercial sources, the working standards must be in n-pentane. The calibration standards for quantitation are specified in TNRCC Method 1005. Additional n-alkane marker standards are needed in this method to define the fractions listed in Table 1.

- Petroleum Product Calibration Standard for Total Petroleum Hydrocarbons, Aliphatic and Aromatic Fractions: Prepared 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. This is the calibration standard for TNRCC Method 1005.

- Approximate Boiling Point /Carbon Number Distribution Marker Standard (and Optional Aliphatic Check Stock Standard): The stock standard can be prepared by accurately weighing approximately 0.01 g (recorded to the nearest 0.0001 g) of individual n-alkanes [n-hexane (nC_6) through n-octacosane (nC_{28}) and n-pentatriacontane (nC_{35})] and diluting to volume with n-pentane in a 50 mL volumetric flask. This solution is diluted 1:10 with n-pentane. The approximate concentration of this stock solution is 20 µg/mL per component. Table 2 lists the boiling points of the n-alkanes. The laboratory should determine the retention times. At a minimum, the standard should contain nC_6, nC_7, nC_8, nC_{10}, nC_{12}, nC_{16}, nC_{21}, nC_{28} and nC_{35} which are the required markers for this method. Purchased standards can also be used and diluted, as appropriate with n-pentane.

- Aromatic Fractionation Check Stock Standard: The stock standard can be prepared by accurately weighing approximately 0.01 g (recorded to the nearest 0.0001 g) of each of the target PNAs. (it should also include lighter aromatics such as benzene, toluene, ethylbenzene, o,m,p-xylene and cumene etc.) and diluting to volume with n-pentane in a 50 mL volumetric flask. This solution is diluted 1:10 with n-pentane. The approximate concentration of this stock solution is 20 µg/mL per component. Purchased standards can also be used and diluted as appropriate.

- Petroleum Products Reference Standards: To assist in the qualitative determination of product type or "fingerprint" of a possible petroleum product(s), it is

recommended that a library of chromatograms be generated of gasoline, kerosene, diesel, motor oil, crude oils and any other pertinent product for comparison purposes. A recommended concentration range is 1000 to 5000 ppm. These may be obtained from several chromatography supply vendors. Typical chromatograms of several petroleum products are included in the Appendix.

7.0 SAMPLE COLLECTION, PRESERVATION, CONTAINERS, AND HOLDING TIMES

Follow guidelines in TNRCC Method 1005. A summary of pertinent information is listed below.

Soil samples should be collected in preweighed VOA vials with PTFE lined caps if the samples are suspected to contain hydrocarbons in the nC_6 to nC_{12} boiling point/carbon range. If hyrdrocarbons within that boiling point/carbon range are not suspected, the soil sample can be collected in wide-mouth glass jars. Soil samples can also be collected and transported in core sampling devices that are designed to be hermetically sealed. Samples are stored at 4˚C from the time of collection until extraction. The extract can be held tightly capped at -15°C for 28 days from the day of collection.

Water samples - Refer to TNRCC Method 1005.

8.0 PROCEDURES

8.1 Sample Extraction

Refer to TNRCC Method 1005 for extraction procedure.

8.2 Extract Fractionation

Fractionate the extract into aliphatic and aromatic components by the following procedure:

- Prepare the column by placing approximately 1 cm of moderately packed glass wool at the bottom of the column. Assemble the stopcock making sure that it turns smoothly.

- Fill the column with about 10 mL of dichloromethane. Add approximately 3 grams of activated silica gel to the column. Ensure that it is packed uniformly by gently tapping the side of the column. Top the column with approximately 0.5 cm of sodium sulfate. Then rinse the column with at least 10 additional mL of dichloromethane. Let the solvent flow through the column until the head of the liquid in the column is just above the top of the column (sodium sulfate nearly exposed). Discard the eluted dichloromethane. Add about 2 mL of n-pentane.

Open the stopcock and let the solvent flow until the liquid in the column is just above the top of the column. Add 10-20 mL of n-pentane in the same manner just described**.** Open the stopcock and let the n-pentane flow until the head of the liquid is just above the top of the column. Discard the eluant. The column is ready for use. The column may be used for fractionating additional samples after rinsing with 10-20 mL of dichloromethane followed by 2 mL of n-pentane and then 10-20 mL n-pentane.

Note: The performance of the silica gel is dependent on the particular lot number of silica gel from the manufacturer, the humidity of the laboratory environment, and the activation temperature. Each laboratory may need to raise or lower the activation temperature depending on their particular conditions to achieve optimal separation.

- Add 1 mL of the sample extract to the column. Open the stopcock and start collecting the eluant immediately in a 10 mL Kuderna-Danish concentrator tube or an equivalent graduated vial. When the head of the n-pentane extract nearly reaches the top of the silica gel column, add n-pentane to the column in 1-2 mL increments while continuing to collect the eluant. It is best to add the solvent gently in a nearly dropwise fashion with a pipette or wash bottle allowing the solvent to run down the inner wall of the column. Continue this approach until approximately 10 mL of the eluant is collected. Label this fraction "aliphatics".

- Once the 10 mL of the n-pentane (aliphatic) fraction has been collected, use another Kuderna-Danish concentrator tube, or an equivalent graduated vial, to begin collecting the aromatic fraction by elution of dichloromethane. This is done in the same manner as above by collection of the eluant immediately after addition of the dichloromethane in 1-2 mL increments or dropwise. **It is critical that the first 3-4 mL be added carefully and slowly.** Once 10 mL have been collected, label this fraction "aromatics". A 1:1 mixture of dichloromethane and acetone can be used to elute aromatics in some cases if difficulties are encountered with the recoveries of the heavier aromatic fractions.

- Fractionation of neat petroleum products, crude oil and wastes is done by directly placing 1 drop of the sample on the silica gel column, or by weighing approximately 0.01 g of the sample, adding 1 mL of n-pentane, and then proceeding with the fractionation as described above.

- When necessary, the 10 mL extracts may be reduced in volume to 1 mL **by the nitrogen blowdown technique**, transferred to an autosampler vial, capped and stored at -15^{o}C until analysis. The samples must be reextracted and refractionated if they are taken to dryness. **A very slow nitrogen blowdown is necessary to minimize loss of volatiles. No heating is allowed**. Concentration to 1 mL is necessary to achieve the detection limits of 50 mg/kg for soil and 5 mg/L for

water. If the TPH concentration obtained from analysis using TNRCC Method 1005 is above 5000 mg/kg in soil and 500 mg/L in water, then volume reduction and concentration to 1 mL of the aliphatic and aromatic fractions is not necessary.

- Silica gel capacity has not been determined. It is recommended that extraction concentrations not exceed 10,000 mg/L.

The fractionation check standards (Section 6) and the blank, LCS, matrix spike and matrix spike duplicate samples must also be fractionated with the sample batch.

8.3 Another Fractionation Approach

A fractionation approach has been developed since the initial development of this method. It is basically the same approach but it uses a larger silica column that is more robust and less susceptible to overloading. This column uses 11 grams of activated silica gel (100/200 mesh, activated at 185˚C for 8 hours) slurried with dichloromethane topped with 1 gram of alumina (5% deactivated) and 0.5 gram of sodium sulfate. The column is conditioned with 10 mL of n-pentane. The sample is loaded as indicated in this method for the smaller column. The aliphatic fraction is eluted with 18 mL of n-pentane and the aromatic fraction is eluted with 21 mL of 1:1 n-pentane and dichloromethane mixture.

8.4 Gas Chromatography

- Gas Chromatographic Conditions: Refer to TNRCC Method 1005 for specific GC conditions.

- Retention Time Windows: Retention time windows can be determined in two ways.
  - Calculate the standard deviation of each individual compound's retention time. Refer to SW-846 8000B Section 7.6 for instructions.

  - A default window may be chosen. This approach is preferred over the one above because capillary columns are reliable with sufficient overall long-term stability to maintain retention time appropriately. This approach is also extremely simple. A window of ± 0.1 minutes should be adequate.

The laboratory should reassess retention time windows for each standard on each GC column and whenever a new GC column is installed.

The aliphatic and aromatic fractions are defined using n-alkanes as markers for the approximate boiling point/carbon number range of interest using GC. These marker compounds are defined in Table 1.

For a given range, such as >nC_8 to nC_{10}, the retention time (RT) window is defined as beginning immediately after elution of the first marker compound (nC_8) or 0.1 minutes after its RT and ending 0.1 minutes after the RT of the ending marker compound (nC_{10}). This means that nC_8 is not included in this range and nC_{10} is included in the range. The same approach for setting up RT windows is used for the other fractions. The exception is nC_6 which is its own fraction and the window should be set at its RT ± 0.1 minutes or calculated as defined in SW-846 8000B Section 7.6.

8.5 Calibration

- External Standard Calibration Procedure: Guidance is provided for calibration and calculations using calibration factors in TNRCC Method 1005. The same calibration curve used in TNRCC Method 1005 should be used for quantitation of the fractions (TPH, aliphatic hydrocarbons and aromatic hydrocarbons) generated using this method. This calibration factor can also be used to calculate the concentration of hydrocarbons present within the n-alkane markers used for defining the approximate boiling point/carbon number distribution. Alternatively, the boiling point distribution can be obtained from normalization of the entire chromatogram (nC_6 to nC_{35}) and determination of area percent within n-alkane markers. It is best to use a chromatographic data system to handle these calculations. A separate calibration file with the additional retention times should be established for the hydrocarbon ranges of interest to determine the approximate boiling point distribution and/or selected hydrocarbon ranges, both total and fractionated.

The use of internal standards and surrogates may be considered but care must be taken to avoid potential biases in quantitation.

- Continuing Calibration Verification: Before analysis can begin, the working calibration factor or calibration curve must be verified on each working day by the injection of a mid-point calibration standard. If the concentration or response for these standards varies from the standard value or predicted response by more than ± 25%, a new calibration curve should be prepared. In addition, it is advisable to check instrument performance further by analysis of a low concentration standard.

$$\% \text{ Difference} = \frac{MCF - CF_V}{MCF} \times 100$$

Where: MCF = Mean calibration factor from the initial calibration
CF_V = Calibration factor from verification standard

8.6 Product Type Identification

Chromatographic peaks with characteristic fuel fingerprints eluting between the solvent front and C_{12} may indicate the presence of gasoline range. Peaks between nC_{12} and nC_{25} can possibly indicate the presence of diesel range compounds. Patterns that do not resemble either product should be noted. Weathering of petroleum hydrocarbons in the environment can greatly alter hydrocarbon distribution.

Product type can be determined by visual inspection of the chromatograms. Chromatograms can become more complicated if crude oil, jet range material, or other refined products are also present. Changes upon weathering must also be considered. However, it may still be possible to determine that the contamination is due to some sort of petroleum product. Industrial solvents can interfere in the analysis; however, the chromatographic fingerprints would be noticeably different. The best approach to maximize the probability of a correct identification is to analyze reference fuels from the sample location, if available, along with the sample. These reference fuels can also be used as calibration standards if desired.

Decisions should be made by the analyst to determine cutoff points for quantitation of different product ranges when contamination is caused by a combination of sources. For example, if soils are contaminated with gasoline range and diesel range materials, there is an area of overlap where certain hydrocarbon ranges are common to both types of petroleum products. A compromise cutoff for mixtures of gasoline with diesel fuel range material is jet fuel/kerosene. There is no appropriate cutoff for a mixture of gasoline with jet fuel/kerosene or mixtures of jet fuel/kerosene with diesel since there is a great deal of overlap of these products. Crude oil contamination also contains a wide range of materials. In cases where mixed products are present, it is perhaps best not to quantitate how much is due to what type of product but to simply quantitate total hydrocarbons and state the approximate carbon range observed.

This method is best suited for analysis of materials up to diesel range. Heavier materials can be detected with a qualitative identification of product type but may not be quantitated effectively since portions of the material may be outside of the range measured by the method (or $>C_{35}$). The analyst should note in the report that heavier material may be present in a test sample.

Additional information on hydrocarbon pattern interpretation is included in some of the references cited.

8.7 Gas Chromatographic Analysis

Samples are analyzed by GC/FID as stated in TNRCC Method 1005.

8.8 External Standard Calculations

For the external standard calibration procedure see TNRCC Method 1005.

8.9 Calculation of Approximate Boiling Point/Carbon Number Distribution:

The approximate boiling point/carbon number distribution is calculated by normalization of sums of peak areas of portions of the chromatograms eluting between preselected retention times corresponding to carbon ranges as indicated in Table 2.

9.0 QUALITY CONTROL

9.1 General Requirements and Recommendations

Refer to TNRCC Method 1005.

- The aromatic and aliphatic fractionation check standard should be analyzed prior to reporting data by this method and with each batch of silica gel to document fractionation efficiency.

9.2 Minimum Instrument QC

Refer to TNRCC Method 1005.

9.3 Initial and Periodic Method QC Demonstration

The following should be conducted as an initial demonstration of laboratory capability, prior to the analysis of any samples. Subsequent to this initial demonstration, additional demonstrations should be conducted on a periodic basis, in response to changes in instrumentation or operations, and/or in response to confirmed or suspected systems, method, or operational problems.

- Initial Accuracy and Precision: Refer to TNRCC Method 1005 for demonstration of initial proficiency.

- Method Detection Limits: Refer to TNRCC Method 1005.

- Fractionation: The stock solutions described in Section 6 should be used to demonstrate the capability of properly fractionating aliphatic and aromatic hydrocarbons in a sample.

For the aliphatic and aromatic check standard, the sum of the fractionated carbon ranges should be 60-140% of the non-fractionated value for the aliphatic fraction and aromatic fraction, respectively. If the aliphatic and aromatic check standards are mixed and fractionated together, then the sum of the aromatic and the aliphatic fractions should also be 60-140% of the TPH obtained using TNRCC 1005.

It is acceptable to encounter a 10-20% crossover of the fractions. This means that it is within the acceptance criteria for this method to have 10-20% aliphatics in the aromatic fraction and 10-20% aromatics in the aliphatic fraction. Chromatograms indicating adequate and poor fractionation are included in the Appendix.

NOTE: **It is critical that extreme care be taken on the elution of aliphatic and aromatic fractions to optimize the fractionation process. This optimization can be achieved by allowing the extract to elute from the column as much as possible before the addition of additional solvent. Add additional solvent in small increments to the column to separate and obtain the fractions in narrow bands.**

The amount of n-pentane and dichloromethane used to elute the aliphatic and aromatic fractions, respectively can be optimized experimentally. Use enough n-pentane to elute all the aliphatics. For the aromatic fraction, use enough dichloromethane to ensure that all the aromatic compounds, especially the PNAs, have eluted from the column.

Other solvent combinations can be used provided that adequate separation and recovery of aliphatics and aromatics can be demonstrated and the procedure used is documented by the laboratory.

Each silica gel batch must be tested after preparation by running a laboratory control fractionation sample.

9.4 Ongoing Method QC Demonstrations

If any of the performance standards specified in Section 9.5 are not met, the problem should be corrected before further samples are analyzed. Any samples run between the last QC samples that meet the criteria and those QC samples that did not meet the acceptance criteria should be rerun. If this is not possible, the data associated with the QC samples not meeting acceptance criteria should be qualified by the laboratory and reported as suspect.

9.5 Quality Control Samples

QC Check Frequency criteria	Frequency	Criteria
Method Blank	1 per analytical batch	< MQL
Aliphatic and Aromatic Fractionation Check Standards	1 per each batch of silica gel	60-140% Recovery <10-20% Crossover
Laboratory Control Sample (LCS)	1 per analytical batch	60-140% Recovery or Lab Established

Matrix Spike (MS)/Matrix Spike Duplicate (MSD)	1 set per analytical batch	60-140% Recovery or Lab Established RPD ±20%

Fractionation should be repeated for any recoveries outside of QC limits. Matrix spike recoveries outside of QC limits should be noted in a case narrative. The QC samples are fractionated into the aliphatic and aromatic ranges and percent recoveries are based on the percent recovery reported from the TNRCC 1005 analytical batch. See Appendix for example calculations. (TO BE DONE).

9.6 Instrument Quality Control

Refer to TNRCC Method 1005 for guidelines.

9.7 Instrument Calibration

Refer to TNRCC Method 1005 for guidelines.

9.8 Daily Mid-Point Calibration

Refer to TNRCC Method 1005 for guidelines.

10.0 DATA REPORTING

Reporting requirements are outlined in TNRCC Method 1005. Additional reporting guidelines are as follow:

- Report the concentration of non-fractionated TPH in the nC_6 to nC_{35} range. Report the concentration of aliphatic and aromatic TPH fractions by the approximate boiling point/carbon number distribution as defined in Table 1.
- Report the method quantitation limits for the total TPH and the aliphatic and aromatic hydrocarbon fractions.
- Chromatograms and data tables, if requested.

11.0 METHOD PERFORMANCE

The method has been applied to the analysis of neat crude oil, gasoline, JP-4, and diesel. In addition, the method has been used for the analysis of soil samples impacted with crude oil and with petroleum products with different degrees of weathering. Recoveries are typically 80% or better for most samples.

Performance evaluation on this method to date by several laboratories is as follows:

- average accuracy of 80% with overall RSD of 6%
- average accuracy of 111% with overall RSD of 10%
- average accuracy of 86% and overall RSD of 21%
- average accuracy of 96% and overall RSD of 18%

Additional method refinement and evaluation are in progress.

The reporting limit per range is influenced by the number of peaks in the range. This is inherent to petroleum hydrocarbons or any complex mixtures. It is estimated to be 10 mg/kg or lower for soil and 1 mg/L or lower for water.

12.0 HEALTH, SAFETY, POLLUTION PREVENTION AND WASTE MANAGEMENT

Refer to TNRCC Method 1005 for guidelines.

13.0 REFERENCES

1. USEPA Test Method for the Evaluation of Solid Waste (SW-846), 3rd Edition, **1996**.
2. 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.**
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Appendix

- **Table A: n-Alkane Marker Compounds, BTEX and PAHs: Approximate Elution Order Within Fractions**

- **Figure A: Typical Chromatograms of Petroleum Products**

- **Figure B: Chromatograms Showing Proper Fractionation of Aliphatics and Aromatics**

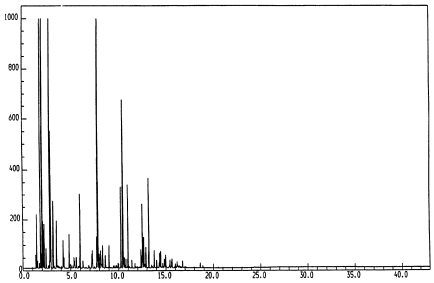
- **Figure C: Chromatograms Showing Poor Fractionation of Aliphatics and Aromatics**

TABLE A : n-Alkane Marker Compounds, BTEX and Target PAHs. Carbon Number, Equivalent Carbon Number and Boiling Points. Note that Equivalent Carbon Number indicates approximate elution of the compounds. Actual elution order may vary and some of the heavier PAHs may not exactly follow the Equivalent Carbon correlation because of different interactions with the chromatographic phases used. The order of elution of late eluting PAHs may be somewhat different. **NOTE: The determination of these individual COCs must be done using EPA Methods 8021/8260 (BTEX) and 8270 (PAHs). The information provided here is to indicate where these compounds elute with respect to the n-alkane markers.**

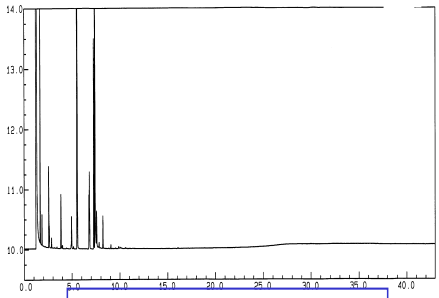
Name and Approximate Order of Elution in a Boiling Point Column like DB-1	Actual Carbon Number	Boiling Point, ˚C	Equivalent Carbon Number (EC)	EC	Name and Approximate Order of Elution in a Slightly More Polar Column like DB-5
nC_6	6	69	**6**	**6**	**nC_6**
Benzene	6	80	6.50		Benzene
nC_7	7	98	**7**	**7**	**nC_7**
Toluene	7	111	7.58		Toluene
nC_8	8	126	**8**	**8**	**nC_8**
Ethylbenzene	8	136	8.50		Ethylbenzene
m-Xylene	8	139	8.60		m-Xylene
p-Xylene	8	138	8.61		p-Xylene
o-Xylene	8	144	8.81		o-Xylene
1,2,3-Trimethylbenzene	9	169	9.84		1,2,3-Trimethylbenzene
nC_{10}	10	174	**10**	**10**	**nC_{10}**
Naphthalene	10	218	11.69		Naphthalene
nC_{12}	12	216	**12**	**12**	**nC_{12}**
Acenaphthylene	12	270	15.06		Acenaphthylene
Acenaphthene	12	278	15.50		Acenaphthene
nC_{16}	16	287	**16**		Fluorene
Fluorene	13	295	16.55	**16**	**nC_{16}**
Anthracene	14	340	19.43		Phenanthrene
Phenanthrene	14	339	19.36		Anthracene
Pyrene	16	360	20.80		Fluoranthene
nC_{21}	21	357	**21**		Pyrene
Fluoranthene	16	375	21.85	**21**	**nC_{21}**
Benzo(a)anthracene	18	435	26.37		Benzo(a)anthracene
Chrysene	18	448	27.41		Chrysene
Benzo(b)fluoranthene	20	481	30.14		Benzo(b)fluoranthene
Benzo(k)fluoranthene	20	481	30.14		Benzo(k)fluoranthene
Benzo(e)pyrene	20	493	31.17		Benzo(e)pyrene
Benzo(a)pyrene	20	495	31.34		Benzo(a)pyrene
Dibenz[a,h]anthracene	22	524	33.92		Indeno[1,2,3-cd]pyrene
Benzo(g,h,i)perylene	21	525	34.01		Dibenz[a,h]anthracene
nC_{35}	35	499	**35**		Benzo(g,h,i)perylene

Name and Approximate Order of Elution in a Boiling Point Column like DB-1	Actual Carbon Number	Boiling Point, ˚C	Equivalent Carbon Number (EC)	EC	Name and Approximate Order of Elution in a Slightly More Polar Column like DB-5
Indeno[1,2,3-cd] pyrene	21	536	35.01	**35**	**nC_{35}**

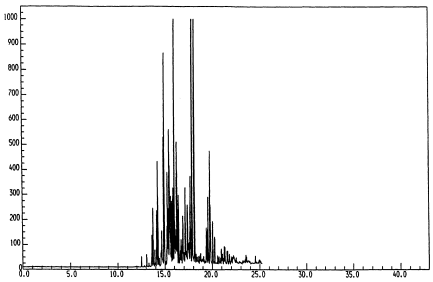
Figure A: Typical Chromatograms of Petroleum Products



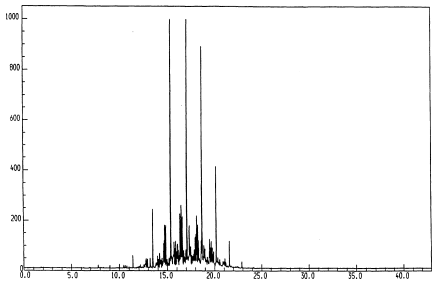
Fresh Gasoline



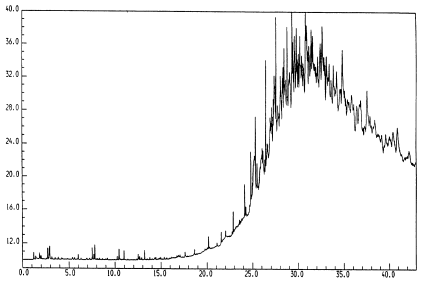
Aviation Gasoline



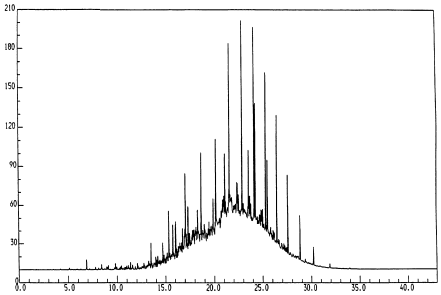
Weathered Gasoline



Jet A



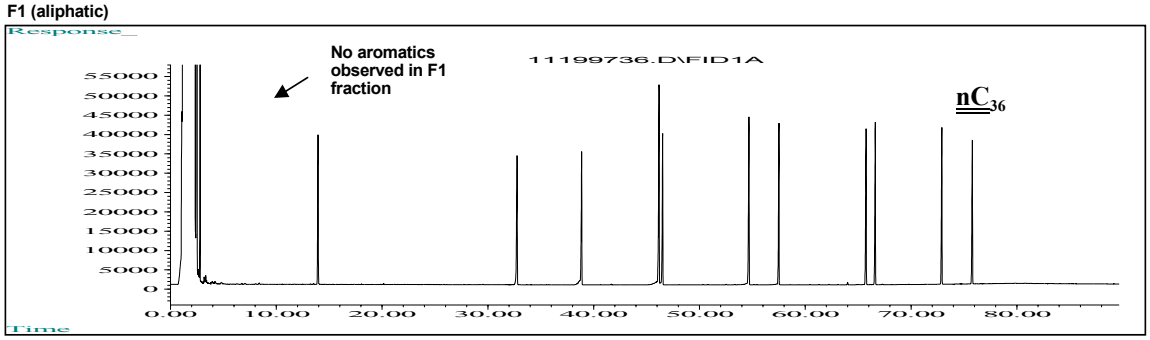
New Motor Oil



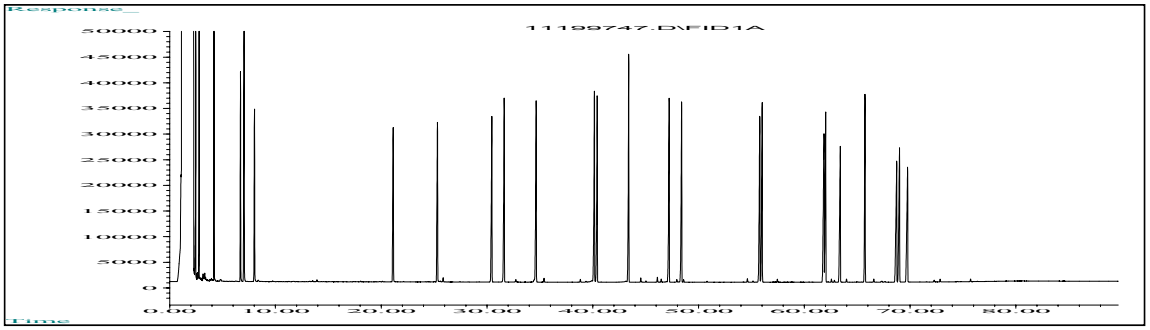
Diesel

Figure B: Chromatograms Showing Proper Fractionation of Aliphatics and Aromatics

F1 (aliphatic)

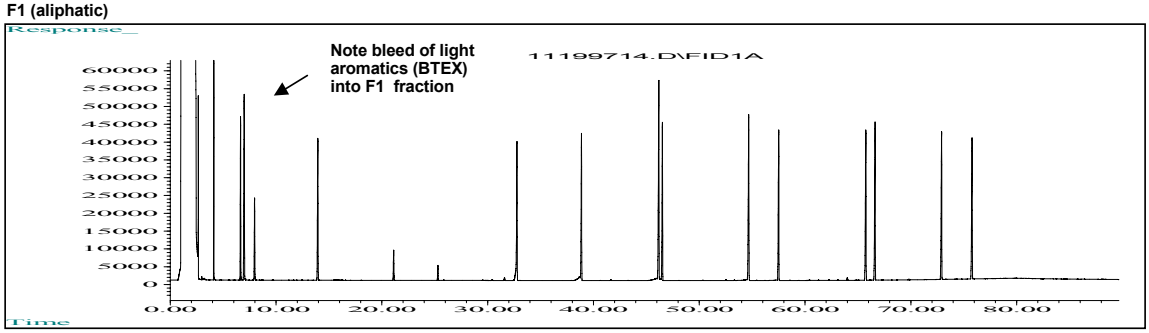


F2 (aromatic)



nC36

F1 (aliphatic)



F2 (aromatic)

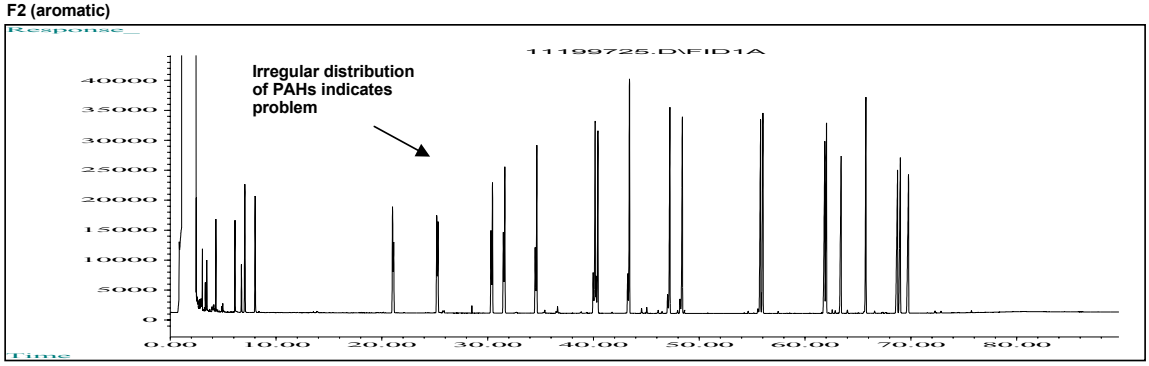


Figure C: Chromatograms Showing Poor Fractionation of Aliphatics and Aromatics