KANSAS METHOD FOR THE DETERMINATION OF LOW-RANGE HYDROCARBONS (LRH)

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Editorial Note: This method is in large part a modification of the Massachusetts Department of Environmental Protection's "Method for the Determination of Volatile Petroleum Hydrocarbons (VPH)." We want to thank that agency for graciously allowing their work to be utilized by others. Since the VPH method has enjoyed a significant amount of direct use by several states, it was determined that it would be best to use it as the base document to establish a method to meet the requirements of the Kansas Department of Health and Environment's Bureau of Environmental Remediation Policy for petroleum cleanup (Policy # BER-041). As needed/warranted, it is expected that this method may be periodically updated as it becomes utilized in Kansas.

DISCLAIMER

Mention of trade names or commercial products does not constitute endorsement by the Kansas Department of Health and Environment (KDHE). Equipment and materials cited in this method may be replaced by similar products, as long as adequate data exist or have been produced documenting equivalent or superior performance.

KANSAS METHOD FOR THE DETERMINATION OF LOW-RANGE PETROLEUM HYDROCARBONS

KANSAS DEPARTMENT OF HEALTH & ENVIRONMENT

1.0 SCOPE & APPLICATION

1.1 This method is designed to measure the total concentrations of low-range hydrocarbons (LRH) in water and soil/ sediment matrices. These volatile hydrocarbons are collectively quantitated from C_5 through C_8. This hydrocarbon range corresponds to a boiling point range between approximately 36°C and 220°C.

1.2 This method is based on a purge-and-trap, gas chromatography (GC) procedure using a Flame Ionization Detector (FID). It is recognized that a GC/Mass Spectrometry (GC/MS) system may also be used if it meets the requirements of this method. This method should be used by, or under the supervision of, analysts experienced in the use of purge-and-trap systems and gas chromatographs. Analysts should be skilled in the interpretation of gas chromatograms and their use as a quantitative tool.

1.3 This method is intended to generate data that may be compared to reporting and cleanup standards promulgated in the Kansas Department of Health and Environment Bureau of Environmental Remediation Policy # BER-041 for low-range hydrocarbons.

1.4 Petroleum products suitable for evaluation by this method include gasoline, mineral spirits, and certain petroleum naphthas. This method, in and of itself, is not suitable for the evaluation of kerosene, jet fuel, heating oils, lubricating oils, and/or other petroleum products which contain a significant percentage of hydrocarbons heavier than C_8.

1.5 The Reporting Limit (RL) of this method for the collective hydrocarbon range is approximately 5-10 mg/kg in soil/ sediment and approximately 100-150 µg/L in water.

1.6 Like all GC procedures, this method is subject to a "false positive" bias in the reporting of individual analytes, in that non-targeted hydrocarbon compounds eluting or co-eluting within a specified retention time window may be falsely identified and/or quantified. Confirmatory analysis by a GC/mass spectrometry (GC/MS) procedure or other suitable method is recommended in cases where an individual analyte reported by this method exceeds an applicable reporting or cleanup standard, and/or where co-elution of a non-targeted hydrocarbon compound is suspected.

1.7 This method is one way to quantify collective concentrations of volatile petroleum hydrocarbons within a specified carbon-number-range. It has been designed in a manner that attempts to strike a reasonable balance between analytical method performance and utility. In this manner, assumptions and biases have been structured into the method to help ensure protective, though not overly conservative data.

As an example, the KDHE recognizes that branched alkanes have lower boiling points than their n-alkane counterpart, while many of the cycloalkane constituents of gasoline range volatile organics have higher boiling points than their n-alkane counterpart. As a consequence:

(1) Depending upon the specific chromatographic column used, most branched C_9 alkanes are expected to elute before n-nonane and will be conservatively counted in the more toxic C_5 through C_8 hydrocarbon range;

(2) Depending upon the specific chromatographic column used, most branched C_5 alkanes will elute before n-pentane, the beginning marker compound for the C_5 through C_8 hydrocarbon range, and will not be counted at all in the C_5 through C_8 hydrocarbon range; and

(3) Depending upon the specific chromatographic column used, most cycloalkanes within the C_5 through C_8 hydrocarbon range will be counted within their proper range.

2.0 SUMMARY OF METHOD

2.1 Samples are analyzed using purge-and-trap sample concentration. The gas chromatograph is temperature programmed to facilitate separation of organic compounds. Detection is achieved by a flame ionization detector (FID) in series. Quantitation is based on comparing the FID response of a sample to a standard comprised of aromatic and aliphatic hydrocarbons. The FID chromatogram is used to determine the collective concentration of hydrocarbons within the C_5 through C_8 range.

2.2 This method should be suitable for the analysis of waters, soils, sediments, wastes, sludges, and light non-aqueous phase liquid (LNAPL) samples. However, it should be noted that the source methods were validated only for soil and water matrices. Water samples may be analyzed directly for volatile petroleum hydrocarbons by purge-and-trap concentration and gas chromatography. Soil/sediment samples are dispersed in methanol to dissolve the volatile organic constituents. An aliquot of the methanol extract is then analyzed by purge-and-trap GC.

2.3 This method is based on (1) USEPA Methods 5030B, 5035A, 8000B, 8021B, and 8015B, SW-846, "Test Methods for Evaluating Solid Wastes", (2) Draft "Method for Determination of Gasoline Range Organics", EPA UST Workgroup, November, 1990; (3) "Modified GRO Method for Determining Gasoline Range Organics ", Wisconsin Department of Natural Resources, PUBL-SW- 140, 1992, and (4) "Method for the Determination of Volatile Petroleum Hydrocarbons (VPH)", Massachusetts Department of Environmental Protection, Rev 1.1, May 2004.

3.0 DEFINITIONS

3.1 **Analytical Batch** is defined as a group of field samples with similar matrices which are processed as a unit. For Quality Control purposes, if the number of samples in such a group is greater than 20, then each group of 20 samples or less is defined as a separate analytical batch.

3.2 **Calibration Standards** are defined as a series of standard solutions prepared from dilutions of a stock standard solution, containing known concentrations of each analyte and surrogate compound of interest.

3.3 **Continuing Calibration Standard** is defined as a calibration standard used to periodically check the calibration state of an instrument. The continuing calibration standard is prepared from the same stock solution as calibration standards, and is generally one of the mid-level range calibration standard dilutions.

3.4 **C_5 through C_8 Hydrocarbons** are defined as all hydrocarbon compounds which contain between five and eight carbon atoms and are associated with the release of a petroleum product to the environment. In this LRH method, C_5 through C_8 hydrocarbons are defined and quantitated as compounds which elute from n-pentane (C_5) to just before n-nonane (C_9).

3.5 **Field Duplicates** are defined as two separate samples collected at the same time and place under identical circumstances and managed the same throughout field and laboratory procedures. Analyses of field duplicates give a measure of the precision associated with sample collection, preservation, and storage, as well as laboratory procedures.

3.8 **Laboratory Control Sample (LCS)** is defined as a reagent water blank (when associated with aqueous samples) or clean methanol blank (when associated with soil/sediment samples) fortified with a matrix spiking solution. The LCS is prepared and analyzed in the same manner as a sample and its purpose is to determine the bias of the analytical method.

3.9 **Laboratory Control Sample Duplicate (LCSD)** is defined as a reagent water blank (when associated with aqueous samples) or clean methanol blank (when associated with soil/sediment samples) fortified with a matrix spiking solution. The LCSD is prepared separately from the LCS but is prepared and analyzed in the same manner as the LCS. The analysis of LCS duplicates provides a measure of the precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.10 **Laboratory Method Blank (LMB)** is defined as an aliquot of reagent water (when associated with aqueous samples) or clean methanol (when associated with soil/sediment samples) spiked with a surrogate standard. The laboratory method blank is prepared and analyzed in the same manner as a sample, exposed to all glassware, solvents, reagents, and equipment. A laboratory method blank is analyzed with every batch of samples, to determine if method analytes or other interferences are present in the laboratory environment, reagents, or equipment.

3.11 **Matrix Duplicates** are defined as split samples prepared and analyzed separately with identical procedures. For soil/sediment samples, matrix duplicate samples are taken from the same sampling container. For aqueous samples, a separate container is used for the matrix duplicate sample. The analysis of matrix duplicates gives a measure of the precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.12 **Matrix Spike (MS) Sample** is defined as an environmental sample which has been spiked with a matrix spiking solution containing known concentrations of method analytes. The purpose of the MS sample is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined through the separate analyses of an unspiked sample aliquot. The measured values in the MS sample must be corrected for background concentrations when calculating recoveries of spiked analytes.

3.13 **Matrix Spiking Solution** is defined as a solution prepared from a separate source than used for the calibration standards, containing known concentrations of method analytes.

3.14 **System Solvent Blank (SSB)** is defined as an aliquot of organic-free water (ASTM Type I reagent grade) and purge-and-trap grade, or equivalent, methanol. For water samples 4.0 uL of methanol is mixed with 5.0 mL of water and for soil samples 100 uL of methanol is mixed with 4.9 mL of water. The SSB is analyzed in the same manner as a sample, exposed to all glassware, solvents, reagents, and equipment. Surrogates must not be spiked into SSBs. An SSB provides one way of determining the level of noise and baseline rise attributable solely to the analytical system, in the absence of any other analytes or non-analytical related contaminants.

3.11 **Low-Range Hydrocarbons (LRH)** are defined as the collective fraction of hydrocarbon compounds eluting from n-pentane to just before n-nonane.

3.19 **Low-Range Hydrocarbon (LRH) Standard** is defined as a 5 component mixture of the 4 compounds and one surrogate listed in Table 1. The compounds comprising the LRH Standard are used to (a) define the individual retention times and chromatographic response factors for each of these individual LRH Analytes, (b) define and establish the windows for the collective hydrocarbon range of interest, and (c) determine average calibration factors or generate calibration curves that can in turn be used to calculate the collective concentration of hydrocarbons within these ranges.

3.20 All other terms are as defined in the most current version of SW-846, "Test Method for Evaluating Solid Waste," USEPA or TNI standard.

Table 1. Low-Range Hydrocarbon (LRH) Standard

Compound	Retention Time (minutes)[1]	
		FID
n-Pentane		7.00
2-Methylpentane		8.65
2,2,4-Trimethylpentane		13.42
n-Nonane		24.11
2,5-Dibromotoluene (surrogate)		35.21

[1]Results obtained using an RTX-502.2 column and chromatographic conditions described in Sections 6.3 and 9.2, respectively

4.0 INTERFERENCES

4.1 Samples can become contaminated by diffusion of volatile organics through the sample container septum during shipment and storage or by dissolution of volatiles into the methanol used for preservation. Trip blanks prepared from both reagent water (when associated with aqueous samples) and methanol (when associated with soil/sediment samples) should be carried through sampling and subsequent storage and handling to serve as a check on such contamination.

4.2 Cross-contamination can occur whenever a low-concentration sample is analyzed immediately after a high-concentration sample. To reduce carryover, the sample syringe and/or purging device must be rinsed between samples with reagent water or solvent. For volatile samples containing high concentrations of water-soluble materials, suspended solids, high boiling-point compounds or organohalides, it may be necessary to wash the syringe or purging device with a detergent solution, rinse with distilled water, and then dry in an oven at 105°C between analyses. The trap and other parts of the system are also subject to contamination; therefore, frequent bake-out and purging of the entire system may be required. A screening step is recommended to protect analytical instrumentation. Whenever an unusually concentrated sample is encountered, it must be followed by

the analysis of a system solvent blank or laboratory method blank to check for cross-contamination. However, due to the potential for samples to be analyzed using an autosampler, the ability to perform this blank analysis may not always be possible. If the sample analyzed immediately after the unusually concentrated sample is free from contamination, then the assumption can be made that carryover or cross-contamination is not an issue. However, if this sample did detect analytes which were present in the unusually concentrated sample, reanalysis is required for all samples analyzed after this highly concentrated sample which detected similar analytes.

5.0 HEALTH AND SAFETY ISSUES

The toxicity and carcinogenicity of each reagent used in this method have not been precisely defined. 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. The laboratory is responsible for maintaining a current file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets should also be made available to all personnel involved in the chemical analysis.

6.0 APPARATUS AND MATERIALS

6.1 The following glassware is used in this method:

6.1.1 VOC Vials: Wide mouth 60-mL VOC vials or 40-mL VOC vials with Teflon/silicone septa for soil/sediment; 40-mL VOC vials with Teflon/silicone septa for waters.

6.1.2 Class "A" Volumetric flasks: 10-mL, 50-mL, 100-mL, and 1,000-mL with a ground-glass stopper.

6.2 Analytical balance: An analytical balance capable of accurately weighing 0.0001 g must be used for weighing standards. A top-loading balance capable of weighing to the nearest 0.1 g must be used for weighing soil/ sediment samples.

6.3 **Gas Chromatography**

6.3.1 Gas Chromatograph: An analytical system complete with temperature programmable gas chromatograph and purge-and-trap concentrator. The data station must be capable of storing and reintegrating chromatographic data and must be capable of determining peak areas using a forced baseline projection.

6.3.2 Chromatographic Column: The required column is: 105 m x 0.53 mm I.D. Restek RTX-502.2 with 3 micron film thickness, or column with equivalent chromatographic properties.

NOTE: The choice of chromatographic column may have a significant impact on the apportionment and quantitation of compounds within the fractional range specified in this method. Substitution of the required column is allowed, only if it can be demonstrated that the selected column has equivalent chromatographic properties and retention times for the compounds and range of interest.

To demonstrate equivalency of column chromatography, a neat gasoline standard must be analyzed on both the required column and the proposed substitute column, with all other run and system parameters held constant. The concentrations of C_5 - C_8 Hydrocarbons must be determined for each column. The Relative Percent Difference between the concentrations obtained for each column must be equal to or less than 25%.

6.3.3 Detectors: The method requires the use of a Flame Ionization Detector (FID).

NOTE: A GC/MS detector may be substituted for FID only if it can be demonstrated to produce equivalent results for the compounds and range of interest. Equivalency should be demonstrated as described above.

6.3.4 Purge-and-trap (P&T) system: The purge-and-trap system consists of a sample purging chamber, a concentrating trap, and a thermal desorber. Complete systems are available commercially.

6.3.4.1 The purging chamber must be designed to accept 5 mL samples with a water column at least 3 cm deep. Purging devices larger than 5 mL have a reduced purging efficiency and should not be used. The gaseous headspace between the water column and the top of the vessel should be at least 3 cm deep. The gaseous headspace between the water column and the trap must have a total volume of less than 15 mL. The purge gas must pass through the water column as finely divided bubbles with a diameter of less than 3 mm at the origin. Fritted glass or needle sparge cells may be used. If needle sparge cells are used, the purge gas must be introduced no more than 5 mm from the base of the water column. Alternate sample purging devices may be used, provided an equivalent performance is demonstrated.

6.3.4.2 The recommended trap should be at least 25 cm long and have an inside diameter of at least 0.105 inches. The trap should be packed with 400 mg of Carbopack B (Supelco Cat. No. 2-0273). Alternative trap packing materials include: Tenax GC (or equivalent); 7.6 cm Carbopack B and 1.3 cm Carbosieve S-III (Supelco Cat No. 2-0321); 7.7 cm Carbopack C and 1.2 cm Carbopack B (Supelco Cat No. 2- 1064); or equal volumes of Tenax, silica gel, and charcoal as described in EPA SW-846 Method 5030B. In general, Carbopack trap packing materials are recommended because they have less of a tendency to retain methanol, which could interfere with the elution of pentane and quench the FID flame. The recommended trap length and packing materials may be varied as long as equivalent performance (i.e., meeting QC criteria of method) has been verified.

6.3.4.3 Prior to initial use, the Carbopack B trap should be conditioned overnight at 270°C by backflushing with an inert gas flow of at least 20 mL/min. Vent the trap effluent to a hood, not to the analytical column. Prior to daily use, the trap should be conditioned for 10 min. at 260°C with backflushing. The trap may be vented to the analytical column during daily conditioning; however, the column must be run through the temperature program prior to analysis of samples. Devices other than the traps recommended in Section 6.3.4.2 should be conditioned and desorbed according to the manufacturer's guidelines.

6.3.4.4 The desorber should be capable of rapidly heating the trap to 260°C.

6.4 Ultrasonic bath.

6.5 Disposable pipets: Pasteur.

6.6 Syringes: 5-mL Luerlock glass hypodermic and 5-mL gas-tight syringe with shutoff valve.

6.7 Syringe valve: Two-way, with luer-lock connections.

6.8 Microsyringes: 1-µL, 5-µL, 10-µL, 25-µL, 100-µL, 250-µL, 500-µL, and 1,000-µL.

6.9 Spatula: Stainless steel.

6.10 Drying oven.

6.11 Dessicator.

7.0 REAGENTS AND STANDARDS

7.1 **Reagents**

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

7.1.2 Solvent: methanol; purge-and-trap grade or equivalent. Store away from other solvents.

7.2 **Stock Standard Solution**

Prepare stock standard solutions in methanol at approximately 10 micrograms per microliter (µg/µL), or purchase certified solutions. Preparation of stock standards and component standards should be done using volumetric glassware.

7.2.1 The stock standard solution consists of the 4 LRH component standards listed in Table 1 and a surrogate standard. Prepare the stock standard solution by accurately weighing approximately 0.1000 g of each LRH Component Standard (listed in Table 2) and the surrogate standard. Dissolve each compound in methanol and dilute to volume in a 10-mL volumetric flask.

7.2.1.1 Place about 8 mL of methanol in a 10-mL tared ground-glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 min. or until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

7.2.1.2 Using a 500-µL syringe, immediately add the required volume of each Component Standard and surrogate to the flask, then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

7.2.1.3 Dilute to volume, stopper, and then mix by inverting the flask three times. Calculate the concentration in µg/µL from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard, provided such purities are certified by the manufacturer or by an independent source.

7.2.1.4 Transfer the stock standard solution into a Teflon-lined screw-cap or crimp cap bottle. Store, with minimal headspace, at -10°C to -20°C and protect from light.

7.2.2 A separate stock standard solution containing only the surrogate must be prepared. Prepare and store this solution using the procedure listed in Section 7.2.1.

7.2.3 Stock standard solutions must be replaced after 6 months, or sooner if comparison with check standards indicates a problem.

7.3 Primary Dilution Standard

Using the stock standard solutions, prepare primary dilution standards in methanol, as needed. The primary dilution standards should be prepared at the concentration shown in Table 2. These standards should be stored with minimal headspace, at -10°C to -20°, and should be checked frequently for signs of degradation or evaporation. The primary dilution standards should be replaced at least monthly.

Table 2. Recommended Primary Dilution Standard

Component	Concentrations, µg/mL
Pentane	100
2-Methyl pentane	100
2,2,4-Trimethylpentane	100
n-Nonane	100
2,5-dibromotoluene (surrogate)	100

7.4 LRH Calibration Standards

Prepare LRH Calibration standards in reagent water from the primary dilution standard (in methanol) at a minimum of five concentration levels (i.e., 1x, 5x, 25x, 100x and 200x). The lowest concentration (1x) determines the minimum working range of the calibration curve and defines the Reporting Limit (RL) for individual analytes. The highest concentration (200x) defines the maximum upper working range of the calibration curve. Individual analytes may not be reported above this concentration without sample dilution. RLs for the hydrocarbon range are discussed in Section 12.0.

7.4.1 Rapidly inject an accurate volume of the primary dilution standard into the water in the expanded area of a filled 10-mL or 100-mL volumetric flask, depending on the calibration standard concentration. Remove the needle quickly after injection.

7.4.2 Mix aqueous standards by inverting the flask three times.

7.4.3 Discard the solution contained in the neck of the flask, and fill the sample syringe from the standard solution contained in the expanded area of the flask.

7.4.4 Do not use pipettes to dilute or transfer samples or aqueous standards.

The recommended concentrations for calibration standards are provided in Table 3. Aqueous standards are not stable and should be discarded after one hour.

Table 3. Recommended LRH Calibration Standard Concentrations

Component	Nominal Concentration (µg/L)				
Pentane	1	5	25	100	200
2-Methylpentane	1	5	25	100	200
2,2,4-Trimethylpentane	1	5	25	100	200
n-Nonane	1	5	25	100	200
2,5-Dibromotoluene (surrogate)	1	5	25	100	200

7.5 Surrogate Standard

The analyst must monitor both the performance of the analytical system and the effectiveness of the method in dealing with sample matrices by spiking each sample, blank, LCS, LCSD, and matrix spike with a surrogate standard. The surrogate standard is included in the LRH calibration standard solutions. The recommended surrogate standard is 2,5-dibromotoluene, which elutes after all compounds of interest. However, other surrogates may be used as long as they are adequately resolved from the components of interest.

7.5.1 Surrogate Spiking Solution: From a stock standard solution prepared as in Section 7.2.2, prepare a surrogate spiking solution at 50 µg/mL in methanol. Add 4.0 µL of this surrogate spiking solution directly into the 5-mL syringe with every aqueous sample, blank, LCS, LCSD, and matrix spike. Add 1.0 mL of the surrogate spiking solution to soil/sediment samples during the extraction step (See Section 9.1.3.2). The use of higher concentrations are permissible and advisable when spiking highly contaminated samples.

7.6 Matrix Spiking Solution

The recommended matrix spiking solution, consisting of the full analyte list (LRH Component Standard), is prepared in methanol at a nominal concentrations of 50 µg/mL.

7.7 Petroleum Reference Standard (To demonstrate equivalency of column chromatography)

The Petroleum Reference Standard consists of an API or commercial gasoline standard. Prepare Petroleum Reference Standard Spiking Solutions by accurately weighing approximately 0.0100 g of neat product. Dissolve the neat product in methanol and dilute to volume in a 100-mL volumetric flask.

8.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

8.1 Aqueous Samples

8.1.1 Aqueous samples should be collected in duplicate (or the number of vials directed by the laboratory) without agitation and without headspace in contaminant-free 40 mL glass VOC vials with Teflon-lined septa screw caps. The Teflon liner must contact the sample. All samples must be chemically preserved as follows:

Samples analyzed with ambient purge temperature: Samples must be acidified to a pH of 2.0 or less at the time of collection. This can generally be accomplished by adding 3 or 4 drops (0.1 to 0.2 mL) of 1:1 HCl (1 part reagent water and 1 part concentrated HCl) to a 40-mL sample vial. Samples must be cooled to 4°C ± 2ºC immediately after collection.

8.1.2 A chain-of-custody form must accompany all sampling vials and must document the date and time of sample collection and preservation method used. The pH of all water samples must be determined by the laboratory after sample analysis has been completed. The pH measurement may be performed on leftover sample. Any acid-preserved sample found to contain a pH above 2 must be so noted on the laboratory report.

8.1.3 A reagent water trip blank, preserved in the same manner as the samples, should accompany each batch of water samples.

8.1.4 Any sample received by the laboratory that is not packed in ice or cooled to 4°C ± 2ºC must be so noted on the laboratory report. The temperature of the cooler must be recorded by the laboratory upon receipt.

8.1.5 Aqueous samples must be analyzed within 14 days of collection.

8.2 **Soil/Sediment Samples**

8.2.1 Soil/sediment samples must be collected in a manner that minimizes sample handling, environmental exposure and/or aeration. The use of specially designed air-tight collection samplers or a 30-mL plastic syringe with the end sliced off is recommended. All soil/sediment must be removed from the glass threads of the vial to ensure an adequate seal. Samples must be cooled to 4°C ± 2ºC immediately after collection.

8.2.2 **Methanol preservation of soil/sediment samples is mandatory.** Methanol (purge-and-trap grade) must be added to the sample vial before or immediately after sample collection. In lieu of the in-field preservation of samples with methanol, soil samples may be obtained in specially-designed air tight sampling devices, provided that the samples are extruded and preserved in methanol within 48 hours of collection.

8.2.3 The desired ratio of soil/sediment-to-methanol is 1 gram soil/sediment to 1 mL methanol/, +/- 25%. The exact weight of the soil/sediment sample and volume of methanol must be known or ascertained by the laboratory when calculating and reporting soil/sediment concentration data. A recommended practice is for a laboratory to provide labeled, pre-weighed sampling vials with the measured volume of methanol clearly indicated to the field sampling technician. The laboratory "fill line" indicating the height of the methanol meniscus should be permanently marked on the side of the sampling container. After the soil sample is added to the methanol in the sampling container, the sample "fill line" indicating the height of the sample-displaced (increased) methanol level should also be marked by the field sampling technician. **In all cases, the soil/sediment sample in the vial must be completely covered by methanol.**

8.2.4 Samples should be collected in duplicate 60-mL or 40-mL VOC vials with Teflon-lined septa screw caps. An additional sample of the soil/sediment must also be obtained (without methanol) to allow for a determination of moisture content and dry weight correction factors.

8.2.5 A methanol trip blank should accompany each batch of soil/sediment samples.

8.2.6 A chain-of-custody form must accompany all sampling vials and must document the date and time of sample collection and, where appropriate, the volume of methanol added. Observations of vial leakage must be so noted on the laboratory report.

8.2.7 Any sample received by the laboratory that is not packed in ice or cooled to 4°C ± 2ºC must be so noted on the laboratory report. The temperature of the cooler must be recorded by the laboratory upon receipt.

8.2.8 Soil/sediment samples must be analyzed within 28 days of collection.

8.3 A summary of sample collection, preservation and holding times is provided in Table 4.

Table 4. Holding Times and Preservatives for LRH Samples

Matrix	Container	Preservation	Holding Time
Aqueous Samples (using ambient temperature purge)	40-mL VOC vials w/ Teflon-lined septa screw caps	Add 3 to 4 drops of 1:1 HCl to pH <2; cool to 4°C ± 2ºC	14 days
Soil/Sediment Samples	VOC vials w/ Teflon-lined septa screw caps. 60-mL vials: add 25 g soil/sediment 40-mL vials: add 15 g soil/sediment	1 mL methanol for every g soil/sediment; add before or at time of sampling; cool to 4°C ± 2ºC	28 days

9.0 PROCEDURE

9.1 **Sample Preparation and Purging**

9.1.1 It is highly recommended that all samples be screened prior to analysis. This screening step may be analysis of a soil/sediment sample's methanol extract (diluted), the headspace method (SW-846 method 3810), or the hexadecane extraction and screening method (SW- 846 Method 3820). For soil/sediment samples, headspace screening of the unpreserved vial (obtained for the purposes of determining soil/sediment moisture content) is also an option.

9.1.2 Water Samples

Introduce volatile compounds into the gas chromatograph using a purge-and-trap concentrator.

9.1.2.1 For a manual load system, remove the plunger from a 5-mL syringe and attach a closed syringe valve. Open the sample or standard bottle, which has been allowed to come to ambient temperature, and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. his process of taking an aliquot destroys the validity of the liquid sample for future analysis; therefore, if there is only one 40-mL vial, the analyst should fill a second syringe at this time to protect against possible loss of sample integrity. This second sample is maintained only until such time when the analyst has determined that the first sample has been analyzed properly. Filling one 20-mL syringe would allow the use of only one syringe. If a second analysis is needed from a syringe, it must be analyzed within 24 hours. Care must be taken to prevent air from leaking into the syringe.

Alternatively, commercially-available auto-samplers may be used to automatically introduce a 5.0 mL sample aliquot directly from a 40 mL sampling vial to the system for purging. Follow manufacturer's instructions for operation. In some cases, concentrations of surrogates and/or matrix spikes may need to be modified to accommodate the fixed injection volumes associated with automated sample-introduction systems.

9.1.2.2 If necessary, samples should be diluted prior to injection into the purge chamber. In such cases, all steps must be performed without delay until the diluted sample is in a gas-tight syringe.

9.1.2.2.1 Dilutions may be made in volumetric flasks (10 mL to 100 mL). Select the volumetric flask that will allow for the necessary dilution. Intermediate dilutions may be necessary for highly concentrated samples.

9.1.2.2.2 Calculate the approximate volume of reagent water to be added to the flask selected and add slightly less than this volume of reagent water to the flask.

9.1.2.2.3 Inject the proper aliquot of sample from the syringe prepared in Section 9.1.2.1 into the flask. Aliquots of less than 1 mL are not recommended. Dilute the sample to the mark with reagent water. Cap the flask and invert three times. Repeat the above procedure for additional dilutions. Alternatively the dilutions can be made directly in the glass syringe to avoid further loss of volatiles.

9.1.2.2.4 Fill a 5-mL syringe with diluted sample as in Paragraph 9.1.2.1.

9.1.2.3 Add 4.0 µL of the surrogate spiking solution through the valve bore of the syringe. Close the valves.

9.1.2.4 If matrix spike analysis is to be performed, add 4.0 µL of the matrix spiking solution through the valve bore of the syringe. Close the valves.

9.1.2.5 Attach the syringe valve assembly to the syringe valve on the purging device. Open the syringe valves and inject the sample into the purging chamber.

9.1.2.6 Close both valves and purge the sample for 11 min. Recommended purge-and-trap operating parameters are provided in Table 5.

Table 5. Recommended Purge and Trap Operating Parameters

Purge gas	Helium
Purge gas flow rate (mL/min)	40
Purge time (min)	11.0 ± 0.1
Purge temperature	Ambient
Desorb temperature °C	260
Backflush inert gas flow (mL/min)	15-20

9.1.2.7 At the conclusion of the purge time, attach the trap to the chromatograph (if necessary), adjust the device to the desorb mode, and begin the gas chromatographic temperature program and GC data acquisition. Concurrently, introduce the trapped materials to the gas chromatographic column by rapidly heating the trap to 260°C and backflushing the trap with inert gas between 15 and 20 mL/min for 4 minutes.

9.1.2.8 While the trap is desorbing into the gas chromatograph, empty the purging chamber. Wash the chamber with a minimum of two 5 mL flushes of reagent water (or methanol followed by reagent water) to avoid carryover of pollutant compounds into subsequent analyses.

9.1.2.9 After desorbing the sample, recondition the trap by returning the purge-and-trap device to the PURGE mode. Wait 15 seconds, then close the syringe valve on the purging device to begin gas flow through the trap. The trap temperature should be maintained at 260°C. After approximately 7 to 15 min, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. After a highly concentrated sample, a longer baking time may be necessary. When cool, the trap is ready for the next sample.

9.1.2.10 If the concentration of an analyte or hydrocarbon fraction in a sample exceeds the calibration range, a dilution of the sample is required. If a sample analysis results in a saturated detector response for a compound, the analysis must be followed by a blank reagent water analysis. If the blank analysis is not free of interferences, the system must be decontaminated. Sample analysis may not resume until a blank demonstrates the lack of system interferences.

9.1.2.11 Do not overdilute samples. Ideally, all dilutions should keep the detector response in the upper half of the linear range of the calibration curve.

9.1.2.12 Following sample analysis, measure and record the pH of the remaining sample.

9.1.3 <u>Soil/Sediments</u>

Soil and sediment samples are extracted with methanol. An aliquot of the extract is added to reagent water and introduced into the gas chromatograph using a purge-and-trap concentrator.

9.1.3.1 Weigh the sample vial to 0.1 g on a top loading balance and determine the weight of the soil/sediment sample; this determination requires knowledge of the empty/tared weight of the sample vial and volume/weight of methanol preservative that was added to the sample vial.

9.1.3.2 Add 1.0 mL of the surrogate spiking solution through the septum. The concentration and/or volume of the surrogate spiking solution may need to be increased for samples that are highly contaminated (based upon screening and/or field notes), to prevent dilution to below detectable limits.

9.1.3.3 If matrix spike analysis is to be performed, add 1.0 mL of the matrix spiking solution through the septum.

9.1.3.4 Agitate sample to facilitate adequate mixing of spiking solution(s) .

9.1.3.5 Allow soil/sediment to settle until a layer of methanol is apparent.

9.1.3.6 Using a microliter syringe, withdraw an appropriate aliquot of the methanol extract for sparging through the septum of the container. Sample screening data can be used to determine the volume of methanol extract to add to the 5 mL of reagent water for analysis. All dilutions must keep the response of the major constituents in the upper half of the linear range of the calibration curve.

9.1.3.7 Remove the plunger from one 5.0-mL Luerlock type syringe equipped with a syringe valve and fill until overflowing with reagent water. Replace the plunger and compress the water to vent trapped air. Adjust the volume to allow for addition of the extract (e.g., for 100 µL of extract adjust to 4.9 mL). Pull the plunger to 5.0 mL for addition of the sample extract. Add the volume of methanol extract determined from screening (recommended 100 µL if dilution not required).

9.1.3.8 Attach the syringe valve assembly to the syringe valve on the purging device. Open the syringe valves and inject the sample into the purging chamber. Complete operations as specified in Paragraphs 9.1.2.6 through 9.1.2.11.

9.1.4 Proceed with the analysis as described in Sections 9.2 through 9.5. Analyze all laboratory method blanks and QC samples under the same conditions as that used for samples.

9.1.5 If the responses exceed the calibration or linear range of the system, use a smaller aliquot of methanol or aqueous sample.

9.1.6 Determination of Percent Moisture

9.1.6.1 Soil and sediment results must be reported on a dry-weight basis.

Transfer 5 to 10 g of sample into a tared (± 0.1 g) crucible. This sample must be obtained from a vial or container that does not contain methanol. Dry this 5 to 10 g sample overnight at 105°C, and reweigh (± 0.1 g). Allow to cool in a desiccator before reweighing. Calculate the percent moisture of the sample using the equation provided in Section 9.6.2.1 (Equation 9). Refer to ASTM Method D2216, Determination of Moisture Content of Soils and Sediments, for more detailed analytical and equipment specifications.

9.2 Analytical Conditions

9.2.1 Recommended analytical conditions are presented below. A chromatographic column with equivalent chromatographic properties, as described in Section 6.3.2, or alternative chromatographic conditions may be substituted to improve resolution of volatile petroleum hydrocarbons.

Chromatographic Column:	105 m x 0.53 mm I.D., 3.0 µm Restek Rtx- 502.2
Oven Temperature Program:	Initial oven temperature 45°C, hold time 1 min; to 100 °C @ 3°C/min, hold time 0 min to 160°C @ 8 °C/min, hold time 0 min to 230 °C @ 20°C/min, hold time 7.5 min
Gas Flow Rates:	Carrier gas - Helium @ 12.5 mL/ min Oxidizer - Air @ 350 mL/min Fuel - Hydrogen @ 30 mL/min Make up - Air @ 17.5 mL/min
Injection Port Temperature:	250°C
Column Inlet Pressure:	20 p.s.i.g.
Detector Temperature:	230°C (FID)

9.3 Retention Time Windows

9.3.1 Before establishing retention time windows, optimize the GC system's operating conditions. Make three injections of the LRH Standard over the course of a 72-hr period. Serial injections over less than a 72-hr period may result in retention time windows that are too restrictive.

9.3.2 Calculate the standard deviation of the three absolute retention times for each individual compound in the LRH Standard.

9.3.3 The retention time window is defined as plus or minus three times the standard deviation of the absolute retention times for each compound in the LRH Standard. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

9.3.4 In those cases where the standard deviation for a particular standard is zero, the laboratory should substitute the standard deviation of a closely eluting structurally similar compound to develop a representative statistically-derived retention time window.

9.3.5 The laboratory must calculate retention time windows for each compound in the LRH Standard on each GC column and whenever a new GC column is installed. These data must be retained by the lab.

9.3.6 The LRH retention time (Rt) window is defined as beginning 0.1 minutes before the Rt of the beginning marker compound and ending 0.1 before the Rt of the ending marker compound for the range.

LRH marker compounds and windows are summarized in Table 6.

Table 6. LRH Marker Compounds

Hydrocarbon Range	Beginning Marker	Ending Marker
C_5-C_8 Aliphatic Hydrocarbons (FID)	0.1 min before n-Pentane	0.1 min before n-Nonane

9.4 Calibration

9.4.1 Internal Standard Calibration Procedure

An internal standard calibration procedure is not recommended for this method.

9.4.2 External Standard Calibration Procedure

The use of Calibration Factors (CF) is the preferred approach to determine the relationship between the detector response and the analyte and collective range concentrations. It is also permissible to utilize linear regression to calculate the slope and y-intercept that best describes the linear relationship between the analyte and collective range concentrations and the instrument response using appropriate formulas.

9.4.2.1 Prepare LRH Calibration Standards at a minimum of five concentration levels in accordance with the procedures and specifications contained in Section 7.0.

9.4.2.2 Analyze each LRH Calibration Standard following the procedures outlined in Section 9.5. Tabulate the area responses against the concentration injected. The ratio of area response to the concentration injected, defined as the calibration factor (CF), may be calculated for individual LRH analytes using Equation 1. The percent relative standard deviation (%RSD) of the calibration factor must be equal to or less than 25% over the working range for the analyte of interest, as determined using Equation 2. When this condition is met, linearity through the origin may be assumed, and the average calibration factor is used in lieu of a calibration curve.

Equation 1: Calibration Factor; Individual LRH Analytes

$$Calibration\ Factor\ (CF) = \frac{area\ \ of\ \ peak}{concentration\ purged\ (\mu g / L)}$$

Equation 2: Percent Relative Standard Deviation

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

9.4.2.3 A total calibration factor must also be established for the hydrocarbon range of interest. Calculate the total CFs for C_5-C_8 Hydrocarbons using the FID chromatogram. Tabulate the summation of the peak areas of all components in the fraction (C_5-C_8 Hydrocarbons) against the total concentration injected. The results can be used to calculate the ratio of the peak area response summation to the concentration injected, defined as the CF, for the hydrocarbon range using Equation 3. The %RSD of the calibration factor must be equal to or less than 25% over the working range for the hydrocarbon range of interest, as determined using Equation 2.

<u>Note</u>: Do not include the area of any surrogate standard in calculating a Range CF.

Equation 3: Range Calibration Factor: Hydrocarbon Range

$$Range\ CF = \frac{Area\ summation\ of\ range\ components}{Total\ concentration\ purged\ (\mu g / L)}$$

9.4.2.4 At a minimum, the working calibration factor must be verified on each working day, after every 20 samples, and at the end of the analytical sequence by the injection of a mid-level continuing calibration standard to verify instrument performance and linearity. If the percent difference (%D) for any analyte varies from the predicted response by more than ±25%, as determined using Equation 4, a new five-point calibration must be performed for that analyte. Greater percent differences are permissible for n-nonane. If the %D for n-nonane is greater than 30, note the nonconformance in the laboratory report. It should be noted that the %Ds are calculated when CFs are used for the initial calibration and percent drifts (Equation 6-5, Appendix 6) are calculated when calibration curves using linear regression are used for the initial calibration.

Equation 4: Percent Difference (%D)

$$\%D = \frac{CF_{AVG} - CF_{CC}}{CF_{AVG}}\ x\ 100$$

where:

CF_{AVG} = Average Calibration Factor calculated from initial calibration.

CF_{CC} = Calibration Factor calculated from continuing calibration standard.

9.4.2.5 C_5 through C_8 Hydrocarbons are quantitated on the FID chromatogram.

9.5 **GC Analysis**

9.5.1 Samples are analyzed in a group referred to as an analytical batch. The analytical sequence begins with instrument calibration (initial or continuing) followed by up to 20 samples interspersed with blanks and QC samples and closed with a mid-range continuing calibration standard. The analytical sequence ends when one or more analytical batches have been processed or when any required qualitative and/or quantitative QC criteria are exceeded.

9.5.2 Samples are introduced into the gas chromatograph using a purge-and-trap concentrator.

9.5.3 Water samples are directly injected into the purging chamber using a 5-mL syringe. Soil/sediment samples are extracted in methanol, the methanol extract is mixed with reagent water, and the methanol/water mixture is injected into the purging chamber using a 5-mL syringe.

9.5.4 Establish daily retention time windows for each analyte in the LRH standard. Use the absolute retention time for each analyte in the continuing calibration standard as the midpoint of the window for that day. The daily retention time window equals the midpoint ± three times the standard deviation determined in Section 9.3.

9.5.5 Hydrocarbon ranges of interest are determined by the collective integration of all peaks that elute between specified range "marker" compounds. Due to the variability in software approaches and applications to collective peak area integration, it is recommended that a manual verification be initially performed to document accurate integration.

9.5.6 **When quantifying on a peak area basis by external calibration, total peak area integration for the hydrocarbon range must be <u>from baseline</u> (i.e. must include the unresolved complex mixture "hump" areas).** This is the approach expected for LRH. For the integration of individual LRH analytes, surrogate compounds, and internal standards, a valley-to-valley approach should typically be used, though this approach may be modified on a case-by-case basis by an experienced analyst. In any case, the unresolved complex mixture "hump" areas must <u>not</u> be included in the integration of individual LRH analytes and surrogate compounds.

9.5.7 If individual LRH analytes are to be quantified using this method, and the response for an individual analyte exceeds the linear range of the system, dilute the sample and reanalyze. The samples must be diluted so that all peaks fall within the linear range of the detector.

9.5.8 For other specific analytes eluting in the LRH range, the upper linear range of the system should be defined by peak height measurement, based upon the maximum peak height documented for a standard within the fraction that is shown to be within the linear range of the detector.

9.5.9 Under circumstances that sample dilution is required because either the concentration of one or more of the individual analytes exceed the concentration of their respective highest calibration standard or any peak eluting within the range exceeds the peak height documented for the highest range-specific calibration standard, the Reporting Limit (RL) for each analyte and/or range must be adjusted (increased) in direct proportion to the Dilution Factor (DF). Where:

$$DF = \frac{\text{Sample Aliquot Volume (mL) + Diluent Volume (mL)}}{\text{Sample Aliquot Volume (mL)}}$$

RL for the diluted sample, RL_d:

RL_d = DF X Lowest Calibration Standard for an individual analyte

<u>Analytical Note</u>: Over dilution is an unacceptable laboratory practice. The post-dilution concentration of the highest concentration analyte must be at least 60 - 80% of its highest calibration standard. This will avoid unnecessarily high reporting limits for other individual analytes which did not require dilution.

9.6 Calculations

The concentration of individual analytes and hydrocarbon ranges in a sample may be determined by calculating the concentration of the analyte or hydrocarbon range purged, from the peak area response, using the calibration factor determined in Section 9.4. If linear regression was used for calibration, refer to Appendix 6 for sample concentration calculations.

9.6.1 Aqueous samples

The concentration of a specific analyte or hydrocarbon range in an aqueous sample may be calculated using Equations 5 and 6, respectively.

Equation 5: Aqueous Samples; Individual LRH Analytes

$$\boxed{Conc\ Analyte\ (\mu g/L) = \frac{(A_x)(D)}{(CF)}}$$

Equation 6: Aqueous Samples: Hydrocarbon Ranges

$$\boxed{Conc\ HC\ Range\ (\mu g/L) = \frac{(A_x)(D)}{(Range\ CF)}}$$

where: A_x = Response for the analyte or hydrocarbon range in the sample. Units are in area counts for individual LRH analytes and the hydrocarbon ranges.

D = Dilution factor; if no dilution was made, D = 1, dimensionless.

CF = Average Calibration Factor for individual LRH analyte, determined in Section 9.4.2.2.

Range CF = Average Calibration Factor for hydrocarbon range, determined in Section 9.4.2.3.

9.6.2 **Non-Aqueous Samples (Methanol Extraction)**

The concentration of a specific analyte or hydrocarbon range in a soil or sediment sample may be calculated using Equations 7 and 8, respectively.

Equation 7: Non-Aqueous Samples; individual LRH Analytes

$$Conc\ Analyte\ (\mu g/kg) = \frac{(A_x)(V_t)(D)(V_w)}{(V_i)(W_d)(CF)}$$

Equation 8: Non-Aqueous Samples: Hydrocarbon Range

$$Conc\ HC\ Range\ (\mu g/kg) = \frac{(A_x)(V_t)(D)(V_w)}{(V_i)(W_d)(Range\ CF)}$$

where: A_x, CF, Range CF, and D have the same definition as for aqueous samples, and

V_t = Total volume of methanol extract, mL

Analytical Note: This volume must also include the 1.0 mL surrogate spiking solution added to soil/sediment samples and the volume of water added due to % moisture correction. See Section 9.6.2.2.

V_i = Volume of methanol extract added to reagent water for purge-and-trap analysis, µL.

V_w = Volume of reagent water used for purge-and-trap analysis, µL.

W_d = Dry weight of sample, g (see Equations 9 through 11)

9.6.2.1 Calculation of Dry Weight of Sample

In order to calculate the dry weight of sample purged (W_d), it is necessary to determine the moisture content of the soil/sediment sample, using the procedure outlined in Section 9.1.6. Using the data obtained from Section 9.1.6, W_d is calculated using Equations 9 through 11.

Equation 9: Percent Moisture

$$\%\ Moisture = \frac{g\ wet\ sample - g\ dry\ sample}{g\ wet\ sample}\ X\ 100$$

Equation 10: Percent Solids

$$\%\ Dry\ Solids\ =\ (100)\ -\ (\%\ Moisture)$$

Equation 11: Dry Weight of Sample

$$W_d\ (g)\ =\ (\%\ Dry\ Solids\ /\ 100)(g\ of\ extracted\ sample)$$

9.6.2.2 Data Correction for LRH Individual Analyte and Range Calculations for Methanol Preservation Dilution Effect

Based on the requirements of SW-846 Method 8000C, Section 11.10.05, LRH analytical results for soil/sediment samples must be corrected for the Methanol Preservation Dilution Effect. The potential for under reporting LRH individual analyte and Hydrocarbon Range concentrations is more pronounced as the "as-received" % moisture content of the soil/sediment sample increases, if this correction is neglected.

LRH individual analyte and Hydrocarbon Range concentrations in solid samples preserved with methanol are subject to a systematic negative bias if the potential increase of the total solvent volume during the methanol extraction process is not considered. This increase in extraction solvent volume is a direct result of the solubility of the entrained sample moisture (water) in the methanol. The total solvent volume is the additive sum of the volume of methanol and the entrained sample moisture that partitions into the methanol during extraction. The volume of water partitioned is estimated from the % moisture determination (and the assumption that 1 g of water occupies a volume of 1 mL). This is a conservative correction regarding calculated LRH concentrations because some fraction of the sample's % moisture may not partition into the methanol, due to various physiochemical binding forces. The total solvent/water volume (Vt) is calculated as follows:

Equation 12: Calculation of Solvent/Water Volume

$$\text{mL solvent/water (Vt)} = \text{mL of methanol} + ((\%\ \text{moisture}/100) \times \text{g of sample})$$

This "corrected" Vt value should be substituted directly for the Vt value shown in Section 9.6.2, Equations 7 and 8, above. <u>It should be noted</u> that whether corrected or uncorrected, the Vt value used in Equations 7 or 8 to calculate LRH concentrations must also include the 1.0 mL surrogate spiking solution added to soil/sediment samples.

10.0 QUALITY CONTROL

10.1 General Requirements and Recommendations

10.1.1 Each laboratory that uses this method is required to operate a formal quality control program in accordance with the most current version of the TNI standard. The minimum requirements of this program consist of an initial demonstration of capability (iDOC) and an ongoing analysis of spiked samples to evaluate and document the quality of data. The initial demonstration of capability should be repeated whenever new staff are trained or significant changes in instrumentation or the method (i.e., new extraction method, etc.) are made. The laboratory must maintain records to document data quality. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance standards for the method. When results of sample spikes indicate atypical method performance, a quality control check standard must be analyzed to confirm that the analytical system was in-control when the measurements were performed.

10.1.2 A methanol trip blank or acidified reagent water trip blank **should** continually accompany each soil/ sediment sample or water sample batch, respectively, during sampling, storage, and analysis.

10.1.3 A Laboratory Method Blank must be run after samples suspected of being highly contaminated to determine if sample carryover has occurred.

10.1.4 At a minimum, for each analytical batch (up to 20 samples of similar matrix), a beginning Initial Calibration or Opening mid-range Continuing Calibration Standard, Closing mid-range Continuing Calibration Standard, Laboratory Method Blank, Laboratory Control Sample (LCS) and LCS Duplicate must be analyzed. Matrix Duplicates, Matrix Spike (MS) and/or MS duplicates should be analyzed, at the request of the data user, based upon the nature of the sample. For analytical batches with more than 10 samples, the analysis of an additional mid-range Continuing Calibration Standard should also be considered. However, it should be noted that the analysis of the Continuing Calibration Standard is required prior to sample analysis, after every 20 samples, and at the end of an analytical sequence, at a minimum. The blank and quality control samples fortified with known concentrations and volumes of analytical standards should be carried through the complete sample preparation and measurement processes.

10.1.5 The recommended sequence of analysis is as follows:

(1) Analytical Batch Opening Initial Calibration or mid-range Continuing Calibration Standard **[REQUIRED]**
(2) Analytical Batch Laboratory Control Sample **[REQUIRED]**
(3) Analytical Batch Laboratory Method Blank **[REQUIRED]**
(4) Up to 20 Samples
(5) Matrix Duplicate sample [As requested by data user]
(6) Matrix Spike/MS Duplicate **[REQUIRED]**
(7) Optional mid-range Continuing Calibration Standard (consider after 10 samples)
(8) Analytical Batch Laboratory Control Sample Duplicate [As requested by data user]
(9) Closing mid-range Continuing Calibration Standard after 20 samples and at end of analytical batch **[REQUIRED]**

a. May be used as the Analytical Batch Laboratory Control Sample for the next analytical batch if batches are processed continuously.
b. May be used as Analytical Batch Opening Continuing Calibration for the next analytical batch if batches are processed continuously.

10.1.6 It is recommended that surrogate standard recoveries be monitored and documented on a continuing basis. At a minimum, when surrogate recovery from a sample, blank, or QC sample is less than 70% or more than 130%, check calculations to locate possible errors, check the fortifying standard solution for degradation, and check changes in instrument performance. If the cause cannot be determined, reanalyze the sample unless one of the following exceptions applies:

(1) Obvious interference is present on the chromatogram (e.g., unresolved complex mixture);
(2) Percent moisture of associated soil/sediment sample is >25% and surrogate recovery is >10%; or
(3) The surrogate exhibits high recovery and associated target analytes or hydrocarbon ranges are not detected in sample.

If a sample with a surrogate recovery outside of the acceptable range is not reanalyzed based on any of these aforementioned exceptions, this information must be noted on the laboratory report.

Analysis of the sample on dilution may diminish matrix-related surrogate recovery problems. This approach can be used as long as the reporting limits to evaluate applicable data quality standards can still be achieved with the dilution. If not, reanalysis without dilution must be performed.

10.2 **Minimum Instrument QC**

10.2.1 The n-pentane (C_5) peak must be adequately resolved from any solvent front that may be present on the FID Chromatogram. This is achievable using the recommended chromatographic column and purge-and-trap procedures. Coelution of the m- and p-xylene isomers is permissible if these analytes are being analyzed. All surrogates must be adequately resolved from individual analytes included in the LRH Component Standard.

For the purposes of this method, adequate resolution is assumed to be achieved if the height of the valley between two peaks is less than 25% of the average height of the two peaks.

10.2.2 Retention time windows must be re-established for each individual LRH Analyte each time a new GC column is installed, and must be verified and/or adjusted on a daily basis. (See Sections 9.3 and 9.5.4)

10.2.3 Calibration factors must be developed based upon the analysis of calibration standards prepared at a minimum of 5 concentration levels. The linearity of calibration factors may be assumed if the %RSD over the working range of the curve is less than or equal to 25%.

10.3 **Initial and Ongoing Demonstration of Capability (iDOC)**

An initial demonstration of capability must be conducted, successfully completed and documented prior to reporting any samples by the LRH Method. An iDOC shall be completed each time there is a change in instrument type, personnel, or method. The laboraotry shall also have a documented procedure for ongoing DOC. All DOC procedures shall be performed according to the most current version of the TNI standard.

10.4 Ongoing Method QC Demonstrations

10.4.1 Each sample, blank, LCS, LCSD, MS, and Matrix Duplicate must be fortified with the surrogate spiking solution. Required surrogate recovery is 70% to 130%. At a minimum, when surrogate recovery from a sample, blank, or QC sample is less than 70% or more than 130%, check calculations to locate possible errors, check the fortifying solution for degradation, and check for changes in instrument performance. If the cause cannot be determined, reanalyze the sample unless one of the following exceptions applies:

(1) Obvious interference is present on the chromatogram (e.g., unresolved complex mixture);
(2) Percent moisture of associated soil/sediment sample is >25% and surrogate recovery is >10%; or
(3) The surrogate exhibits high recovery and associated target analytes or hydrocarbon ranges are not detected in sample.

If a sample with a surrogate recovery outside of the acceptable range is not reanalyzed based on any of these aforementioned exceptions, this information must be noted on the laboratory report.

Analysis of the sample on dilution may diminish matrix-related surrogate recovery problems. This approach can be used as long as the reporting limit for the applicable data quality standards will still be achieved with the dilution. If not, reanalysis without dilution must be performed. Recoveries outside of the acceptable range after reanalysis must also be noted on the laboratory report.

10.4.2 At a minimum, with every batch of 20 samples or less the laboratory must analyze the following:

10.4.2.1 **Continuing Calibration Standard** - A mid-range continuing calibration standard, prepared from the same stock standard solution used to develop the calibration curve, must be analyzed prior to sample analysis to verify the calibration state of the instrument. For large analytical batches that contain more than 10 samples, the analysis of an additional mid-range continuing calibration standard is recommended after the analysis of the tenth sample. However, it should be noted that a mid-range continuing calibration standard is required after every 20 samples and at the end of the analytical sequence. If the percent difference or percent drift of any analyte within the continuing calibration standard varies from the predicted response by more than 25%, a new five-point calibration must be performed for that analyte.

10.4.2.2 **Laboratory Method Blank** - A water or soil Laboratory Method Blank is prepared by fortifying a 5 mL reagent water blank with 4 µL of the surrogate spiking solution (for water samples), or by fortifying 25 ml of methanol with 1.0 mL of the surrogate spiking solution (for soil/sediment samples). Peaks must not be detected above the Reporting Limit within the retention time window of any analyte of interest. The hydrocarbon ranges must not be detected at a concentration greater than 10% of the most stringent cleanup standard.

10.4.2.3 **Laboratory Control Sample** - A Laboratory Control Sample is prepared by fortifying a 5 mL reagent water blank with 4 µL of the matrix spiking solution (for water samples), or by fortifying 25 mL of methanol with 1.0 mL of the matrix spiking solution (for soil/sediment samples). The spike recovery must be between 70% and 130%.

10.4.2.4 **Matrix Spike/Matrix Spike Duplicate** - The water or soil matrix spike is prepared by fortifying an actual 5 mL water sample with 4 µL of the matrix spiking solution, or by fortifying an actual 15-25 g soil sample with 1.0 mL of the matrix spiking solution (see Section 7.6). The desired spiking level is 50% of the highest calibration standard. However, the total concentration in the MS (including the MS and native concentration in the unspiked sample) should not exceed 75% of the highest calibration standard in order for a proper evaluation to be performed. The purpose of the matrix spike is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate unspiked aliquot and the measured values in the matrix spike corrected for background concentrations. The corrected concentrations of each analyte within the matrix spiking solution must be within 70 - 130% of the true value.

10.4.3 At the request of the data user, and in consideration of sample matrices and data quality objectives, matrix spikes and matrix duplicates may be analyzed with every batch of 20 samples or less per matrix.

10.4.3.1 **LCS Duplicate** – A Laboratory Control Sample Duplicate is prepared by fortifying a 5 mL reagent water blank with 4 µL of the matrix spiking solution (for water samples), or by fortifying 25 mL of methanol with 1.0 mL of the matrix spiking solution (for soil/sediment samples). The LCS Duplicate is prepared separately from the LCS but prepared and analyzed in the same manner as the LCS and is used as the data quality indicator of precision. The Analytical Batch Precision is determined from the Relative Percent Difference (RPD) of the concentrations (not recoveries) of LCS/LCSD pair. The RPD for individual LRH analytes and hydrocarbon range concentrations must be less than or equal to 25.

10.4.3.2 **Matrix duplicate** - Matrix duplicates are prepared by analyzing one sample in duplicate. The purpose of the matrix duplicates is to determine the homogeneity of the sample matrix as well as analytical precision. The RPD of detected results in the matrix duplicate samples must not exceed 50 when the results are greater than 5x the reporting limit.

10.4.4 If any of the performance standards specified in Section 10.4.1 and 10.4.2 are not met, the cause of the non-conformance must be identified and corrected before any additional samples may be analyzed. Any samples run between the last QC samples that met the criteria and those that are fallen out must be rerun. These QC samples include the opening continuing calibration standard, laboratory method blank, LCS, LCSD, and closing continuing calibration standard. If this is not possible, that data must be reported as suspect.

11.0 DATA PRODUCTION AND REPORTING

11.1 **Calibration**

Using the external calibration procedure (See Section 9.4.2) calibrate the GC as follows:

11.1.1 Using the FID chromatogram, calculate an average CF for the surrogate 2,5-dibromotoluene.

11.1.2 Using the FID chromatogram, calculate an average collective CF for the total concentration of the C_5 - C_8 Hydrocarbons. Tabulate the collective peak area response of the 3 components (n-pentane, 2-methylpentane, 2,2,4-trimethylpentane) against the collective concentration injected.

11.2 **Sample Analysis**

11.2.1 <u>FID Chromatogram</u>

11.2.2.1 Determine the total area count for all peaks eluting 0.1 minutes before the Rt for n-pentane and 0.01 minutes before the Rt for n-nonane. It is not necessary to identify or quantitate individual aliphatic compounds within this range.

11.2.2.2 Determine the peak area count for the surrogate standard 2,5-dibromotoluene.

11.2.2.3 Using the equations contained in Section 9.6, calculate the concentrations of C_5 - C8 Hydrocarbons and the surrogate standard 2,5-dibromotoluene.

11.2.3 <u>Data Adjustments</u>

11.2.3.1 Subtract the <u>area counts</u> of the surrogate compound(s) from the total area count of any range in which they elute. If the recommended surrogate 2,5-dibromotoluene is used, no correction is necessary, as this compound elutes after the range of interest.

12.0 REPORTING LIMITS

The Reporting Limits (RLs) for LRH Analytes shall be based upon the concentration of the lowest calibration standard for the analyte of interest. The RL must be greater than or equal to the concentration of the lowest calibration standard.

The RLs for the hydrocarbon range shall be based upon the concentration of the lowest calibration standard for an individual analyte within the range of interest. The RL will be set at 100x the concentration of the lowest calibration standard for the associated analyte.

Based on a concentration of 1 µg/L for the lowest calibration standard for all analytes, the following reporting limits would be generated for the hydrocarbon ranges:

Aqueous Samples: Hydrocarbon range reporting limits would be equivalent to 100 µg/L.
Soil/Sediment Samples: Hydrocarbon range reporting limits would be equivalent to 5 mg/kg based on a 1:1 ratio of methanol: soil and analysis of a 100 µL aliquot of the methanol extract in 5 mL water.

13.0 REFERENCES

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APPENDIX 1

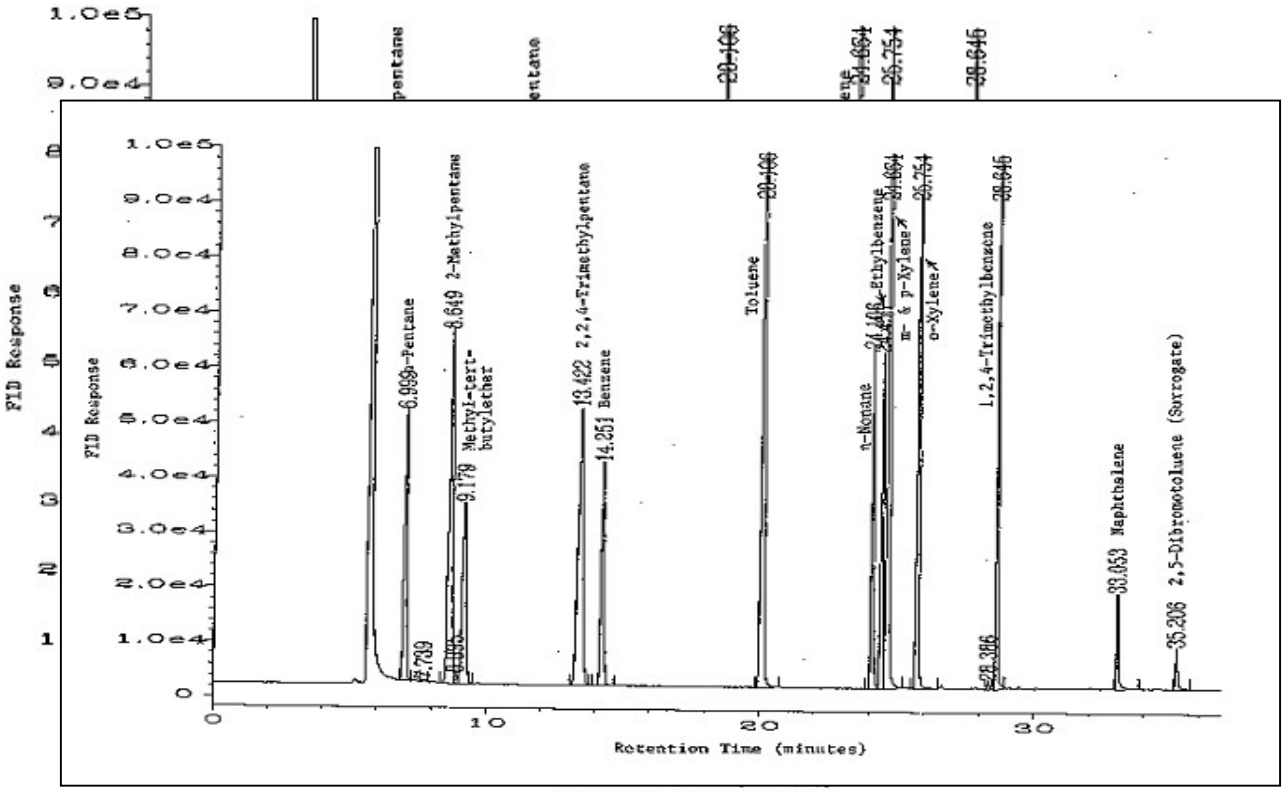
CHROMATOGRAMS

Figure	Description
1	Gas Chromatogram (FID) for VPH Component Standard (20 ug/L Standard)
2	Gas Chromatogram (FID) of the VPH Gasoline Standard

Note: These are representative chromatograms were taken from one of the source methods. The hydrocarbon ranges in the chromatograms are similar, but differ slightly from the ranges required by this method.

Figure 1 Gas Chromatograms of the VPH Component Standard (20 µg/L)

Restek RTX-502.2 capillary column (105 m x 0.53 mm i.d., 3-µm film thickness); PID (10.2 eV) in series with and FID (OI analytical); Tekmar (model 4000) purge-and-trap concentrator fitted with a custom absorbent trap packed with Carbopack B (Supelco); purge-and-trap and GC operating conditions as specified in Section 9.0 of the method. N-dodecane elutes at 31.2 minutes(not shown in chromatogram)



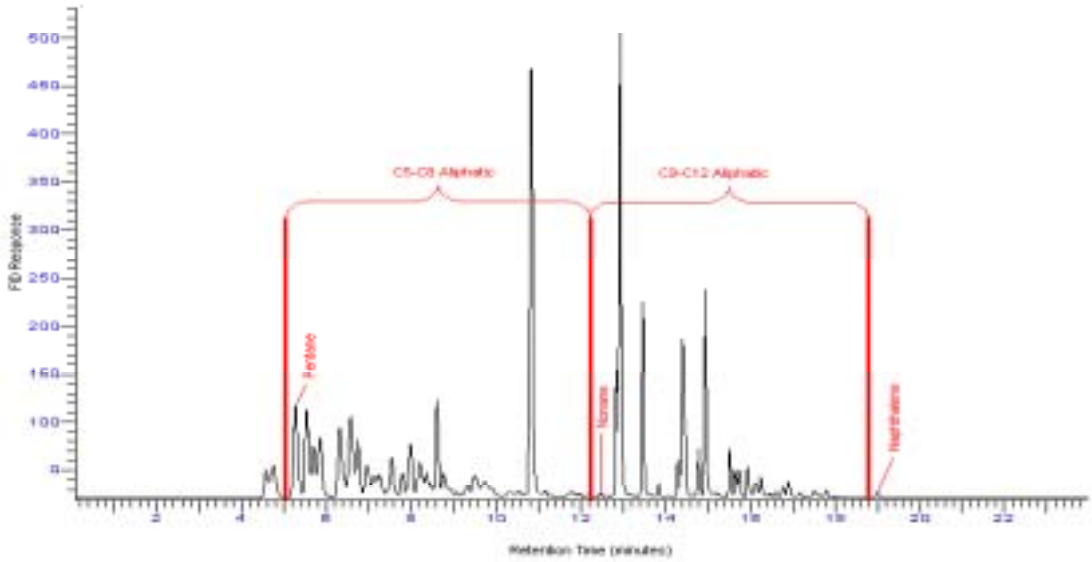


Figure 2 Gas Chromatogram (FID) of the VPH Gasoline Standard

Restek RTX-502.2 capillary column (105-m x 0.53-mm i.d., 3-µm film thickness); PID detector (10.2-eV lamp) in series with an FID detector (O.I. Analytical); Tekmar (model 3000) purge-and-trap concentrator.