ALTERNATIVE METHOD FOR TRPH

Attached is a letter to all laboratories performing work for the Waste Cleanup program, particularly 62-770 and Method FL-PRO. This method is being provided as an alternative to 418.1 and 9073, and does not use freon as the extraction solvent.

This method is written in Word 6.0. The figures are not available with the text. Please call the QA Section at (904) 488-2796 for copies of the figures.

M E M O R A N D U M

TO: Laboratory Directors

FROM: Doug Jones, Bureau of Waste Cleanup
Silky S. Labie, Quality Assurance

DATE: November 1, 1995

SUBJECT: Florida Petroleum Residual Organic (FL-PRO) - an Alternative Method to Total Recoverable Petroleum Hydrocarbons by 418.1 or 9073

The Department identified a need to find more environmentally sensitive replacement methods for the referenced tests because the currently approved methods use freon as a solvent. A Technical Advisory Committee (TAC) was formed during the rule development activities of Chapter 62-770 for the purpose of identifying a suitable method.

The Department expressed the need to have information concerning petroleum products in the diesel and motor oil range. Rather than adopting two or even three methods that would cover this range of product types, the Department and the TAC developed a method that combined several of the commonly used methods so that the targeted range of petroleum could be analyzed in a single method. A state-wide validation study was performed by 13 volunteer laboratories.

FL-PRO utilizes a methylene chloride extraction with analysis by a gas chromatographic equipped with a flame ionization detector (GC-FID).

The Bureau of Waste Cleanup's programs whose rules specify the use of 418.1 or 9073 will now also accept data that has been generated by FL-PRO, and will ultimately amend their rules to require its use. This method is available for immediate use and may be obtained by calling the Quality Assurance Section at (904) 488-2796 and requesting "Method FL-PRO", revised November 1, 1995 or by downloading the method from the Quality Assurance Bulletin Board System, QUASI-BBS.

Laboratories who decide to use this method will need to amend their Comprehensive QA Plan (CompQAP) to include the method in their analytical capabilities. At a minimum, this will require the addition of the method to Section 5.0 of a 15-Section CompQAP or Section 2.0 of a CompQAP that has adopted the Department's Standard Operating Procedures. Amendments to other sections will be required if other changes are made in order to use this method (e.g., purchase of a GC, purchase of sample preparation equipment, etc.).

NOTE: Wastewater facilities may not use this method for TRPH or Oil and Grease. The use of this method is only applicable to the activities of the Bureau of Waste Cleanup that addresses Chapters 62-761, 62-762, 62-770, 62-773 and 62-775, or other corrective actions such as consent orders.

cc: District Waste Program Administrators
BWC Section Administrators
Delegated Counties

FLORIDA DEPARTMENT OF ENVIRONMENTAL PROTECTION

METHOD FOR DETERMINATION OF PETROLEUM RANGE ORGANICS (Method # FL-PRO)

1. Scope and Application

1.1 Analytes

1.1.1 This method is designed to measure the concentration of Petroleum Hydrocarbons in water and soil in the alkane range of C_8 - C_{40}.

1.1.2 The intent is to provide the Florida Department of Environmental Protection with an accurate estimate of petroleum concentration in environmental samples in the above stated C-Range (nominally diesel through motor oils). It cannot be used as an indication of gasoline contamination.

1.2 Quantitation Limits

1.2.1 The MDL of this method is estimated to be at least 4 mg/kg for soil and 0.1 mg/L for water. Each laboratory shall establish a laboratory specific MDL for all matrices prior to analyzing any samples.

1.3 Dynamic Range

Dilutions should be performed as necessary to put the chromatographic envelope within the linear range of the method. Linear range is dependent in part upon column type, detector sensitivity and injection volume. Typically, the approximate range is 170 - 17,000 ng on column of Total PHS (see 7.4.3). Each laboratory must establish and document the linear range for the instrument(s) in use in the laboratory.

1.4 Experience

1.4.1 This method is based on a solvent extraction, gas chromatography (GC) procedure. This method should be used by, or under supervision of, analysts experienced in the use of solvent extractions and gas chromatographs. The analysts should be skilled in the interpretation of gas chromatograms and their use as a quantitative tool.

2. Method Summary

2.1 One liter of water or a specified quantity of soil (extraction method dependent) is spiked with two surrogates and extracted with methylene chloride. The water is removed from the extract, concentrated to a volume of 2.0 mL, and treated with silica gel to remove potential organic interferences. An aliquot is injected onto a capillary column gas chromatograph (GC) equipped with a flame ionization detector (FID). Quantitation is based on the detector response compared to a series of normal alkane standards.

2.2 This method is based in part on USEPA Methods 8000 and 8100, SW-846, "Test Methods for Evaluating Solid Waste", 3rd Edition (1), Method OA-2 (3), work by the EPA UST Work Group "Measurement of Petroleum Hydrocarbons: Report on Activities to Develop a Manual", 1990 (11), Method AK103.0, Revision 2 (12), PUBL-SW-141, July 1993 (13) and the Florida Department of Environmental Protection Technical Advisory Committee for 62-770, F.A.C, Petroleum Contamination Site Cleanup Criteria.

3. Definitions

3.1 Petroleum Hydrocarbons: All chromatographic peaks, both resolved and unresolved, eluting between the peak start of n-octane (n-C_8) and the peak end after n-tetracontane (n-C_{40}). Quantitation is based on direct comparison of the area within this range to the total area of the Petroleum Hydrocarbon standard as determined from FID response using baseline - baseline integration.

3.2 Petroleum Hydrocarbon Standard: A 17-component mix of all even - numbered normal alkanes from C_8 to C_{40} (Table 1). This standard serves as a quantitation standard and a retention time window defining Petroleum Hydrocarbons.

3.3 Sample Matrix Spike: A selected sample from the analytical set spiked with the Petroleum Hydrocarbon Standard and surrogate standards. The calculated spike recovery shall be used as a control and should be between 41-101% for water and an average of 51-215% for soils (see Table 2 for specific sonication or soxhlet criteria).

3.4 Laboratory Control Sample: A reagent water or standard soil (e.g., Ottawa sand) spiked with the Petroleum Hydrocarbon standard and surrogate standards. The calculated spike recovery may be used as a laboratory control and must be between 55-118% for water and an average of 63-143% for soils (see Table 2 for specific sonication or soxhlet criteria).

3.5 Pattern Recognition Standards: Various commercial petroleum products used by a laboratory to identify petroleum product types. These may be purchased from vendors or obtained from commercial sources.

3.6 Other terms are defined in SW-846 and Appendix C of the DEP Manual For Preparing Quality Assurance Plans (DEP-QA-001/90), September 30, 1992 (2).

4. Interferences

4.1 Other organic compounds, including chlorinated hydrocarbons, phenols, and phthalate esters are measurable. As defined in the method, the Petroleum Range Organics method results include these compounds.

4.2 Animal and vegetable oil and grease and biogenic terpenes are also measurable if the sample is not cleaned up before analysis. In order to eliminate false positives from these sources, **the silica cleanup (9.1.6) is a mandatory part of this procedure**.

4.3 High purity reagents (pesticide grade or better) must be used to minimize interference problems.

4.4 Method interferences are reduced by washing all glassware with hot soapy water followed by successive rinses with tap water, acetone, and methylene chloride. At least one reagent blank (see DEP-QA-001/90 for definition) must be analyzed with each batch or for every 20 samples to demonstrate that the samples are free from method interferences.

4.5 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of a solvent blank to check for instrument contamination.

5. Safety Issues

5.1 The toxicity or carcinogenicity of each reagent used in this method has 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 awareness file of Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of Material Safety Data Sheets (MSDS) should also be made available to all personnel involved in the chemical analysis.

Additional references to laboratory safety should be available and should be identified for use by the analyst.

6. Apparatus

6.1 Glassware - All specifications are suggested only.

6.1.1 4 oz. amber glass wide mouth jars with teflon®-lined screw caps (solid samples) and 1 liter amber glass containers with teflon®-lined screw caps (aqueous sample).

6.1.2 Glass separatory funnel - 2000 mL with Teflon® stopcock.

6.1.3 Concentrator tube. Kuderna-Danish (K-D) - 10 mL graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test. Ground glass stopper is used to prevent evaporation of extracts.

6.1.4 Evaporative flask, Kuderna-Danish - 500 mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs or other appropriate attachment devices.

6.1.5 Snyder column, Kuderna-Danish - three ball macro (Kontes K-5030000-0121 or equivalent). Alternatively, a rotary evaporation set-up may also be used.

6.1.6 Vials - Amber glass, 10 to 15 mL capacity, with Teflon®-lined screw cap. Glass vials with teflon®-lined cap suitable for use with a GC auto-sampler.

6.1.7 Disposable pipets: Pasteur

6.1.8 Beakers: 400 mL, 250 mL

6.1.9 Drying column: 20-mm I.D. Pyrex chromatographic column with precleaned, silanized glass wool at bottom and a Teflon® stopcock.

Note: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of precleaned, silanized glass wool to retain the absorbent. Prewash the glass wool pad with 50 mL of acetone followed by the 50 mL of elution solvent prior to packing the column with absorbent.

6.2 Boiling chips - Approximately 10/40 mesh. Heat to 400^{o} for 30 minutes or Soxhlet extract with methylene chloride.

6.3 Microsyringes: 1μL, 5 μL, 10 μL, 25 μL, and 100 μL

6.4 Water bath - Heated with concentric ring cover, capable of temperature control (±2^{o}C). The bath should be used in a hood.

6.5 An analytical balance capable of accurately weighing 0.0001 g should be used for standards. A top-loading balance capable of weighing to the nearest 0.1 g should be used for sample analysis.

6.6 Gas Chromatography

6.6.1 Gas Chromatograph: Analytical system complete with a gas chromatograph and all required accessories, including a Flame Ionization Detector, column supplies, gases, and syringes. A data system capable of determining peak areas using a forced baseline and baseline projection is required. A data system capable of storing and reintegrating chromatographic data is recommended.

6.6.2 Columns

6.6.2.1 Column 1: 30 M X 0.25 mm DB-5 or equivalent, minimum of 0.25 micron film thickness.

6.6.2.2 Alternate Column: 30 M X 0.25 mm DB 17 or equivalent, minimum of 0.25 micron film thickness.

6.6.2.3 Other columns may be used - capillary columns are required to achieve the necessary resolution. Megabore columns may be acceptable if all column performance criteria are met (see 9.2.2). The column must be capable of resolving typical Petroleum components, and the solvent front from C_8.

6.7 Sonication

6.7.1 Ultrasonic cell disrupter: A horn-type sonicator equipped with a titanium tip should be used. A Heat System - Ultrasonics, Inc. Model W-385 (475 Watt) sonicator or equivalent (power wattage must be a minimum of 375 with pulsing capability and No. 200 1/2" tapped Disrupter Horn) plus No. 207 3/4"

Tapped Disrupter Horn, and No. 419 1/8" Standard tapered Microtip probe.

6.7.2 A Sonabox is recommended with the above disrupter for decreasing sound (Heat Systems-Ultrasonics, Inc., Model 432B or equivalent).

6.7.3 Vacuum filtration apparatus

6.7.3.1 Buchner funnel

6.7.3.2 Filter paper: Whatman No. 41 or equivalent

6.8 Soxhlet Extraction

6.8.1 Soxhlet extractor: 40 mm i.d., with 500 mL round bottom flask

6.8.2 Glass or paper thimble and/or contaminant-free precleaned, silanized glass wool

6.8.3 Heating mantle - Rheostat controlled

6.9 Nitrogen evaporator with high purity nitrogen gas source.

6.10 Percent Moisture Determination

6.10.1 Desiccator

6.10.2 Drying Oven

7. Reagents and Standards

7.1 Reagent water: Carbon filtered deionized water shown to be free of all interfering components.

7.2 Methylene chloride, hexane, acetone, chloroform, carbon disulfide - pesticide grade or equivalent.

7.3 Sodium sulfate - (ASC) granular, anhydrous. Purify by heating at 400^{o}C for 4 hours in a shallow tray or extracting three times with methylene chloride and drying at 105^{o}C.

7.4 Stock standard solution - Prepare the following stock standards. Unless noted, all are prepared in the methylene chloride listed in 7.2 above. Standard preparation should follow guidelines in Method 8000.

7.4.1 Recommended Surrogate Standards: 2000 μg/mL ortho-terphenyl (OTP) and 3000 μg/mL nonatriacontane (C_{39}). A working solution is made at 50 μg/mL (OTP) and 300 μg/mL (C_{39}) in acetone (a water soluble solvent). To be added to all samples and quality control samples before extraction and to the standards (see 7.4.3).

7.4.2 Individual stock solutions of C_8 - C_{40} even normal alkanes (see Table 1). For solubility reasons, it may be necessary to prepare stock solutions of n-alkanes in other solvents such as hexane, chloroform, acetone or carbon disulfide.

7.4.3 Petroleum Hydrocarbon Standard: C_8 - C_{40} even normal alkane standards with each component at 500 μg/mL. Suggested calibration levels are 5, 50, 150, 250, 350 and 500 μg/mL of each individual component. This is equivalent to 85, 850, 2550, 4250, 5950 and 8500 μg/mL total alkanes in the standards and **is defined as TOTAL PHS**. The concentration of OTP and C_{39} must remain at a constant 50 and 300 μg/mL level in all concentration levels.

7.4.4 Stock spike-solution: A working solution of Petroleum Hydrocarbon standard in acetone designed to provide a Total PHS concentration in the spiked sample of 5 mg/L in water or 300 mg/kg in soils.

> **Note**: The concentration of the spike in the sample should be approximately 3 - 5 times the level expected in the sample. Therefore, the level of the spike should be adjusted based on knowledge of anticipated sample concentrations.

7.4.5 Silica gel

7.4.5.1 Silica gel solid-phase extraction cartridges (40 μm particles, 60 A pores), 0.5 g, Supelco, J.T. Baker, or equivalent.

7.4.5.2 Silica gel, 60 to 200 mesh, Davidson Grade 950 or equivalent (deactivated with 1 to 2 percent water).

8. Sample collection, Preservation, Containers, and Holding Times

8.1 Whenever possible, samples should be grab samples which are collected directly into the sample container. Sample collection equipment such as bailers or intermediate containers should be avoided (exceptions: collection from monitoring wells or grab samples in surface water at depth). Unless required by permit, automatic samplers may not be used. Pumps such as bladder pumps or peristaltic pumps shall not be used.

8.2 All sampling equipment which contacts the sample shall be constructed of teflon®, stainless steel or glass. Under no circumstances can flexible PVC tubing such as tygon®, be used in the purging or sample collection process.

8.3 Water samples shall be collected in a one liter glass container, soils in a glass jar. All containers shall be sealed with a screw cap with teflon® liner. Water samples shall be acidified to a pH of less than 2 with hydrochloric or sulfuric acid (reagent grade or better).

8.4 The samples shall be stored at $4^{o}C$ from the time of collection until extraction. Extraction shall be performed on waters within seven days of sample collection and on soils within 14 days of sample collection. All analysis must take place within 40 days of extraction.

9. Procedure

9.1 Sample preparation

9.1.1 The sample preparation methods are based on SW-846 Method 3510 (Separatory Funnel Liquid-Liquid Extraction) or Method 3520 (Continuous Liquid-Liquid Extraction) for water and Method 3550 (Sonication) or Method 3540 (Soxhlet Extraction) for soils.

9.1.2 Water extraction - Separatory Funnel

9.1.2.1 Mark the sample bottle at the water meniscus for later determination of sample volume. Pour the sample into a 2 liter separatory funnel. For blanks and laboratory quality control standards, pour 1 liter of carbon filtered water for each quality control sample into separatory funnels.

9.1.2.2 Check and note the initial pH.

9.1.2.3 Add 2 mL each of ortho-terphenyl surrogate standard at 50 μg/mL and C_{39} surrogate at 300 μg/mL to all

samples, spiked samples, duplicates, method reagent blanks and laboratory control samples (see 9.1.2.4).

9.1.2.4 Prepare at least one method reagent blank, one sample matrix spike and either a matrix spike duplicate or duplicate sample, with each batch of 20 samples or less. Laboratory control samples may be added as an additional quality control measure.

9.1.2.5 Add 60 mL methylene chloride (CH_2Cl_2) to the sample bottle and rotate the bottle to rinse the sides. Transfer the solvent to the separatory funnel. Extract the sample by shaking it for two minutes with frequent ventilation.

9.1.2.6 Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample and may include stirring, filtration of the emulsion through precleaned, silanized glass wool, centrifugation, or other physical methods. Collect the solvent extract in an Erlenmeyer flask. If the emulsion cannot be broken (recovery of 80% of the methylene chloride, corrected for the water solubility of methylene chloride), transfer the sample, solvent, and emulsion into the extraction chamber of a continuous extractor and proceed as described in Section 9.1.3.

9.1.2.7 Drain the bottom layer (CH_2Cl_2) into a 250 mL beaker or flask.

9.1.2.8 Repeat the extraction twice more using a 60 mL aliquot of CH_2Cl_2 each time. Collect the solvent in the same container described in 9.1.2.7. Record the volume recovered.

9.1.2.9 Measure the exact volume of the samples by adding tap water to the marked level of each sample container and measuring the volume with a graduated cylinder. Record all volumes.

9.1.2.10 Dry the extract by passing it through a drying column containing about 10 cm of anhydrous sodium sulfate. Collect the dried extract in a Kuderna-Danish (K-D) concentrator. Rinse the Erlenmeyer flask, which contained the solvent extract, with 20-30 mL of methylene chloride and add it to the column to complete the quantitative transfer.

Alternatively, put a plug of precleaned, silanized glass wool in a funnel and fill about 2/3 with Na_2SO_4. Rinse the funnel and Na_2SO_4 with 30-40 mL of CH_2Cl_2, discard. Pour the extract through the Na_2SO_4 into a 500 mL K-D evaporative concentrator. Rinse the beaker then the Na_2SO_4 with small amounts of CH_2Cl_2. Add these rinses to the K-D.

9.1.2.11 Add a boiling chip to the K-D and attach a 3 ball Snyder column to the top. Pre-wet the column by adding about 1 mL of CH_2Cl_2 to the top.

Note: The concentration step is critical; losses can occur if care is not taken.

9.1.2.12 Place the K-D apparatus in a hot water bath (60 - 65^{o}C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 10-20 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

9.1.2.13 If the extract is highly colored or a precipitate forms during concentration, the final volume should be higher (5-10 mL).

9.1.2.14 After the K-D has cooled, rinse the Snyder column and middle flask with a small amount of CH_2Cl_2. Be sure to rinse all of the ground glass joints well, as compounds collect on the ground glass. Final volume should be 2

mL. If it is greater than 2 mL, proceed to 9.1.2.15. If it is 2 mL, proceed to 9.1.2.16.

9.1.2.15 If further concentration is required, add another clean boiling chip to the concentrator tube and attach a two ball micro-Snyder column. Prewet the column by adding 0.5 mL of methylene chloride or exchange solvent to the top of the column. Place the K-D apparatus in a hot water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 5-10 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joints in the concentrator tube with 0.2 mL of extraction solvent. Adjust the final volume to 2.0 mL.

Alternatively, concentrate the extract to 2.0 mL under a gentle stream of nitrogen using the N-evap apparatus. If the extract is highly colored, forms a precipitate, or stops evaporating, the final volume should be higher (5-10 mL). Transfer to a labeled 4 mL (or 12 mL) vial with Teflon®-lined cap, mark the meniscus.

9.1.2.16 Record the prep information for the extraction and concentration steps. Mark the meniscus on the vial, and record the final volume. Proceed to 9.1.6 for cleanup.

9.1.3 Water extraction - Continuous liquid liquid extraction

9.1.3.1 Mount the continuous extractor on appropriate racks.

9.1.3.2 Put 250 mL CH_2Cl_2 in a round bottom flask, add a few boiling chips. Add 300 mL of CH_2Cl_2 to the extractor flask.

9.1.3.3 When pouring water into the extractor, minimize the disturbance of the solvent layer and avoid getting water

into either sidearm by pouring the water down the back of the extractor.

9.1.3.4 Check and note the pH.

9.1.3.5 Mark the sample bottle at the water meniscus for later determination of sample volume. Pour the sample into the continuous liquid liquid extractor. For blanks and laboratory control samples, use 1 liter of carbon filtered water for each quality control sample.

9.1.3.6 Add 2 mL each of ortho-terphenyl surrogate standard at 50 μg/mL and C_{39} surrogate at 300 μg/mL to all samples, spiked samples, duplicates, method reagent blanks and laboratory control samples (see 9.1.3.7).

9.1.3.7 Prepare at least one method reagent blank, one sample matrix spike and either a matrix spike duplicate or duplicate sample, with each batch of 20 samples or less. Laboratory control samples may be added as an additional quality control measure.

9.1.3.8 Add enough carbon filtered water to the extractor flask to allow the solvent in the removable sidearm to just begin to drip into the round bottom flask.

9.1.3.9 Remove the condenser from the rack and wipe the lower joint lip with a laboratory tissue soaked with methylene chloride. Place the condenser on the top of the extractor. Turn on the cool water supply and check the flow indicators.

9.1.3.10 Turn on the heating mantle. Record the starting time on the prep sheet. Check after 15 minutes to be sure that the solvent in the round bottom flask is boiling, that solvent is dripping from the lip on the condenser, and that the volume of the solvent in the round bottom flask is still about 240 mL.

9.1.3.11 Check all extractor joints for leaks with a laboratory tissue. Allow the extraction to proceed for 18-24 hours.

9.1.3.12 Turn off the heating mantle and allow the apparatus to cool (30-60 minutes) with water flowing through the condenser.

9.1.3.13 The solvent contained in the round bottom flask is the extract. Transfer the extract to a 400 mL beaker, rinsing with a small amount of CH_2Cl_2. If the volume of solvent is less than about 250 mL, record the solvent volume.

9.1.3.14 Go to 9.1.2.9 and continue with the preparation.

9.1.4 Soil preparation - Sonication

9.1.4.1 Note the apparent condition of the sample (e.g. presence of foreign materials, variable particle size, presence of sheen, etc.). Remove large rocks or other foreign materials (e.g., glass, metal, etc.) and mix the sample well.

9.1.4.2 Since final numbers are reported as mg/dry Kg, a moisture determination must be made. Pre-weigh an aluminum weighing boat. Weigh 5-10 g of the sample into the boat and record the weight of the boat and the combined weight of the boat and sample on a percent moisture worksheet. Dry the sample in a hood or warm (no greater than $100^oC \pm 5^oC$) oven overnight. Cool in a desiccator until the sample reaches room temperature and weigh for the moisture determination:

$$\% \text{ Moisture} = (A-C)/(A-B) \times 100$$

Where: A = weight of boat + wet sample

B = weight of boat

C = weight of boat + dry sample

Note: Make sure drying oven is placed under a hood. Heavily contaminated soils will produce strong organic vapors which may be detrimental to analysts' health.

9.1.4.3 Weigh a 25 g aliquot of the original sample into a 400 mL beaker or a 250 mL centrifuge bottle (do not use the dried sample from 9.1.4.2). Record weight to the nearest 0.1 g. Add 2 mL each of 50 μg/mL ortho-terphenyl and 300 μg/mL C_{39} to all samples and quality

control samples (see 9.1.4.6). Add spike mixture to selected samples and laboratory control samples. Mix the samples immediately.

9.1.4.4 Add 25 g of dried Na_2SO_4 and stir the mixture well with a stainless steel spatula. The sample should have a free-flowing sandy texture. If it forms a large clump, add more Na_2SO_4 until the proper texture is achieved and note it on the prep sheet.

9.1.4.5 Add 100 mL of CH_2Cl_2 to all samples.

9.1.4.6 Prepare at least one method reagent blank, one sample matrix spike and either a matrix spike duplicate or a duplicate sample with each batch of 20 samples or less. Laboratory control samples (e.g. Ottawa sand) may be used as an additional quality control measure.

9.1.4.7 Sonicate the samples for 3 minutes at an output setting of 10 with the 3/4 inch sonicator for 1/2 inch below the surface of the solvent. The sonicator should be in the 1 second pulse mode, with the duty cycle set a 50%.

> **Note**: Depending on the sonication equipment, a setting of 10 may shatter beakers. If the sonication unit has a demonstrated history of these occurrences, the setting may be lowered to avoid glass breakage. The setting should not be lowered past 7.

9.1.4.8 Decant and filter extracts through Whatman No. 41 filter paper using vacuum filtration or centrifuge and decant extraction solvent.

9.1.4.9 Repeat the extraction two or more times with two additional 100-mL portions of solvent. Decant off the extraction solvent after each sonication. On the final sonication, pour the entire sample into the Buchner funnel and rinse with extraction solvent.

9.1.4.10 Record the total volume of the solvent that is recovered.

9.1.4.11 Go to 9.1.2.10 and continue with the preparation.

9.1.5 Soil Preparation -Soxhlet Extraction

9.1.5.1 Proceed with 9.1.4.1 and 9.4.1.2.

9.1.5.2 Weigh a 10 g aliquot of the sample to the nearest 0.1 g and transfer into the thimble (do not use the dried sample from 9.4.1.2). Add 2 mL each of 50 μg/mL ortho-terphenyl and 300 μg/mL C_{39} to all samples and laboratory quality control samples (see 9.1.5.4). Add appropriate spike to the selected sample(s) and laboratory control samples. Mix samples immediately. Blend 10 g sodium sulfate with the sample. The sample should have a grainy texture - if the sample clumps, add more sodium sulfate until a free-flowing, grainy texture is achieved and note the addition. The extraction thimble must drain freely for the duration of the extraction period. A precleaned, silanized glass wool plug above and below the sample in the Soxhlet extractor is an acceptable alternative for the thimble.

9.1.5.3 Place loaded thimbles in extractors.

9.1.5.4 Prepare at least one method reagent blank, one sample matrix spike and either a matrix spike duplicate or a duplicate sample with each batch of 20 samples or less. Laboratory control samples (e.g. Ottawa sand) may be used as an additional quality control measure.

9.1.5.5 Add 300 mL of methylene chloride to the 500 mL extraction flask. Also add a few methylene chloride washed boiling chips to the flask. Connect the extractor. Allow samples to extract for 18-24 hours, or as long as necessary to achieve optimum surrogate recovery at 4-6 cycles per hour. Be sure that coolant is flowing around the condensers.

9.1.5.6 Allow the extract to cool after the extraction is complete.

9.1.5.7 Go to 9.1.2.10 and continue with the preparation.

9.1.6 Silica gel Cleanup (**mandatory**)

9.1.6.1 Add 0.3 g of loose silica gel to the extract and shake the mixture for 5 minutes, or pass the extract through

0.5 g silica gel solid-phase extraction cartridge conditioned with 5 mL of methylene chloride.

9.1.6.1.1 When using an extraction cartridge the recovered volume of solvent passing through the cartridge must be less than or equal to the recorded extract volume from 9.1.2.16. If it is not, the recovered volume must be used in calculations.

9.1.6.1.2 When using loose silica gel, filter the extract through a plug of precleaned silanized glass wool in a disposable glass pipette or allow to settle and decant extract into appropriate vial.

9.1.6.2 Transfer cleaned extract to a labeled vial with a Teflon®-lined screw cap or sealed Teflon®-lined septum vial for analysis.

9.1.7 Dilution Technique

9.1.7.1 This is used for product or waste samples which are soluble in methylene chloride.

9.1.7.2 Weigh 1 g of sample into a 10 mL volumetric flask. Dilute to 10 mL with methylene chloride. Pass an aliquot of sample through a small (pipet) column of Na_2SO_4 to dry. Proceed to 9.1.6 for silica gel cleanup.

9.2 Gas Chromatography

9.2.1 Conditions (Recommended): Set helium column pressure to 20# or at optimum pressure for column diameter. Set column temperature to 40°C for 1 minute, then 10°C/min to 300°C and hold until the last standard (C_{40}) has eluted so that baseline quantitation is possible (run time averages approximately 60 minutes). Set FID Detector to 300°C and injector to 280°C.

9.2.2 Performance Criteria: GC run conditions and columns must be chosen to meet the following criteria:

9.2.2.1 Resolution of C_8 from the solvent front.

9.2.2.3 The column must be capable of separating typical petroleum hydrocarbon components from the surrogates.

9.3 Calibration

9.3.1 Initial Calibration - Calibration shall be by external calibration using a minimum of a blank and 5 concentration levels for the initial calibration. The standard concentrations shall lie within the linear range of the curve. The lowest standard shall be at a concentration equal to or slightly higher than the practical quantitation limit (4 times the MDL) of the method, the highest concentration shall be near the end of the linear range. Quantitation shall be by calibration factor or linear regression.

In all cases, response of the standards must be determined by continuous integration of **all** responses (**excluding** surrogates) from a forced baseline beginning at a point prior to the elution of C_8 to a point past C_{40} when a heavy motor oil would be expected to return to baseline. All responses must be determined as responses to baseline (see Figures 1 and 2) and not valley to valley (see Figure 3). The selection of the time interval (i.e. time from beginning to end of integration) should be based on injection of appropriate pattern recognition standards and **must be constant for all standards and samples**.

9.3.1.1 Calibration Factor - Determine the area response of the 17 components and calculate the calibration factor of each level as the ratio of area of standard mix against the mass injected:

$$\text{Calibration Factor} = \frac{\text{Total PHS Area}}{\text{Total PHS mass injected (ng)}}$$

PHS - Petroleum Hydrocarbon Standard

PHS Area - Response as integrated in 9.3.1

Total PHS - Refers to the sum of the concentration of the individual components as defined in 7.4.3.

If the percent relative standard deviation of the calibration factor is less than or equal to 20% over the working range, the linearity through the origin can be

assumed and the average calibration factor can be used in place of a calibration curve.

9.3.1.2 Linear Regression - If a calibration factor cannot be used then a linear regression shall be calculated using the area of the total PHS area (see 9.3.1) versus the PHS concentration. The correlation coefficient shall be equal to or greater than 0.995.

9.3.1.3 The accuracy of the initial calibration shall be verified by injecting a midpoint concentration of a standard mix that has been obtained from a different source (i.e., different vendor). The calculated value shall be within ±20% of the expected value.

9.3.1.4 If the initial calibration fails any of the above criteria, a new set of standards shall be prepared, analyzed and evaluated prior to analyzing any samples.

9.3.2 Continuing Calibration - The working calibration factor or calibration curve must be verified on each working day by the injection of a continuing calibration standard (CCS) at a midpoint concentration (250 μg/mL unless the curve has been adjusted from method). This standard must be evaluated prior to the analysis of any samples.

9.3.2.1 If the response for this standard varies from the predicted response by more than ±25%, a new initial calibration curve must be prepared and verified before samples are analyzed (see 9.3.1).

$$\text{Percent Difference} = \frac{R1 - R2}{R1} \times 100$$

where:

R1 = Average CF from the initial calibration curve or standard response from initial calibration curve

R2 = Calibration Factor from CCS or standard response from CCS

9.3.2.2 Retention Time Window - The retention time window for the surrogates and C_8 and C_{40} shall be within the established range (see 9.4.2 below). If they are out of acceptance range, a new initial calibration must be

prepared and verified before samples are analyzed (see 9.3.1).

9.4 Retention Time Window Definition

9.4.1 Before establishing windows, be certain that the GC system is within optimum operating conditions. Make three injections of the method standard throughout the course of a 72 hour period. Serial injections over less than a 72 hour period result in retention time windows that are too tight.

9.4.2 Calculate the standard deviation of the absolute retention times for the two surrogates, C_8, and C_{40}.

9.4.2.1 The retention time window for individual peaks is defined as a plus or minus three times the standard deviation of the absolute retention time for each component.

9.4.2.2 In those cases where the standard deviation for a particular analyte is zero, the laboratory should use ±0.05 min as a retention time window.

9.4.3 The laboratory must calculate retention time windows for these standards on each GC column and whenever a new GC column is installed. The data must be retained by the laboratory.

9.5 Gas Chromatograph Analysis

9.5.1 Samples are analyzed by GC/FID. Suggested injection volumes are 1 - 2 μL using the conditions established in 9.2.

9.5.2 If an initial calibration (9.3.1) has already been performed, verify the calibration by analysis and evaluation of a mid-point CCS (9.3.2) on each working day.

In addition, a continuing calibration standard must be run every 10 samples and at the end of the sequence. The concentration of these should vary, based on the expected sample concentrations, however, at least one must be at a level of 1-2 times the calculated PQL as a verification of sensitivity.

9.5.3 Evaluate the continuing calibration response per 9.3.2.1 and 9.3.2.2. If either performance criteria fails, the instrument must be recalibrated (9.3.1) and all samples which were injected after the failed standard must be reanalyzed.

9.5.4 A methylene chloride blank must be run in every sequence to determine the area generated on normal baseline bleed under the conditions prevailing in the 24 hour period. This area is determined by continuous integration of all responses under the same conditions (i.e. forced baseline and predetermined time interval) as the standards and samples (see 9.3.1 and 9.6). This blank is reported as the solvent blank and its calculated value (PHS concentration) shall be less than the method detection limit of the method. **Do not baseline subtract.**

Methylene chloride blanks should also be run after samples suspected of being highly concentrated to prevent carryover. If the blank analysis shows contamination, the column must be baked out and subsequent blanks analyzed until the system is shown to be free from contaminants.

9.5.5 If the sample concentration exceeds the linear range of the method in the final extract, the extract must be diluted and reanalyzed.

9.5.6 Qualitative Identification (Pattern Recognition): - (Optional)

9.5.6.1 The laboratory may qualitatively identify the petroleum products when reporting data by direct comparison of sample chromatograms to retention times and peak patterns of pattern recognition standards. The experience of the analyst weighs heavily in the interpretation of the chromatogram.

9.5.6.2 Because of weathering, the patterns may not be a perfect match, however, the characteristics of a petroleum hydrocarbon pattern must be present. References 7, 8, 9 and 10 contain some background information on hydrocarbon pattern recognition. Environmental samples may contain more than one type of product, and loss of light end components may mean the product has been in the subsurface a longer period of time.

9.5.6.3 Qualititative information may be reported on the final laboratory report. This information should include an alkane range. If possible, product identification should be included and may be based on the individual laboratory's chromatograms of commercial petroleum products (e.g., diesel, motor oil, etc.).

9.6 Calculations:

The integrated area for **all** peaks eluting from n-octane through n-tetracontane shall be determined using a baseline drawn from the baseline point prior to n-octane to a point past n-tetracontane where the baseline returns to normal (see Figures 1 and 2 and paragraph 2 of 9.3.1). All area including the "hump-a-gram" and surrogate standards shall be included. **Do not** integrate valley to valley for individual peaks (Figure 3). The concentration shall be determined by calibration factor (9.6.1) or linear regression (9.6.2), and the solid samples shall be calculated to report on a dry weight basis (9.6.3).

9.6.1 Calibration Factor:

$$Cs = \frac{(Ax)(Ve)(D)}{(CF)(Inj)(Vs)}$$

Where:

Cs = Concentration of Petroleum Hydrocarbons (mg/L or mg/kg)

Ax = Response for the Petroleum Hydrocarbons in the sample (baseline to baseline integration), units in area

Ve = Volume of final extract (mL)

D = Dilution factor, if dilution was performed on he sample prior to analysis. If no dilution was made, D = 1, dimensionless

CF = Average Calibration Factor from **initial** calibration (See 9.3.1)

Inj = Volume of injected sample (μL)

Vs = Volume of sample extracted in mL (9.1.2.9) or weight of sample in g (9.1.4.3 or 9.1.5.2)

9.6.2 Linear Regression

$Ce = A + BAx$

Where:

Ce = Concentration of Petroleum Hydrocarbons in extract (μg/mL)

Ax = Response for the Petroleum Hydrocarbons in the sample (baseline to baseline integration), units in area

A = y-intercept value

B = Slope

$$Cs = \frac{(Ce)(Ist)(Ve)(D)}{(Inj)Vs)}$$

Where:

Cs = Concentration of Petroleum Hydrocarbons (mg/L or mg/kg)

Ce = Concentration in extract determined from linear regression (μg/mL)

Ist = Amount of each standard injected (μL) - must be constant for all standards

Ve = Volume of final extract (mL)

D = Dilution factor, if dilution was performed on the sample prior to analysis. If no dilution was made, D = 1, dimensionless

Inj = Volume of injected sample (μL)

Vs = Volume of sample extracted in mL (9.1.2.9) or weight of sample in g (9.1.4.3 or 9.1.5.2)

9.6.3 Dry weight determination:

$$\text{mg/dry kg PH} = \frac{Cs}{1-(\%\text{moisture}/100)}$$

Where:

Cs = Concentration of Petroleum Hydrocarbons (mg/L or mg/kg)

10. Quality Control

10.1 The laboratory must establish the ability to generate acceptable accuracy and precision. This should include the analysis of QC check samples plus the calculation of average recovery and the standard deviation of the recovery as outlined in Method 8000, Section 8.0.

10.2 The laboratory must, on an ongoing basis, demonstrate through the analysis and evaluation of quality control check standards and continuing calibration standards (9.5.3) that the operation of the measurement system is in control.

10.3 Each laboratory shall generate control limits based on +/- 3 standard deviations from the average recovery for all spikes and surrogates, and + 3 standard deviations from the average precision value (RPD, RSD or I) for all duplicates. The limits that are generated must be within the criteria specified on Table 2.

10.4 After successful calibration (Section 9.3.1 or 9.3.2 whichever is applicable), analyze the reagent blank sample which must be prepared with every analytical batch or sequence. The surrogate recovery must be within established limits and the calculated TRPH value of the blank shall be at or below the established method detection limit.

10.5 For every batch of 20 samples or less, a matrix spike sample and either matrix spike duplicates or sample duplicates shall be processed, analyzed and evaluated. The accuracy of the spiked samples and the precision of the duplicate samples must be within established limits. Laboratory control samples, if prepared, should also be analyzed.

10.6 If any of the criteria in 10.2, 10.4 or 10.5 are not met, the problem must be corrected before samples are analyzed.

10.6.1 If the matrix spike(s) are not within laboratory or method specified limits, the results of the laboratory control samples

or quality control check samples should be assessed. If the results of the latter two quality control checks are acceptable, the problem with the matrix spike(s) may be attributed to matrix interferences, and the analysis of the sample set may proceed.

10.7 The surrogate standard recoveries in each sample must be calculated. **Unlike the calculation of petroleum hydrocarbons, the response must be based on a valley-valley integration of the peak response.** If recoveries are outside established limits, verify calculations, dilutions, standard solutions and instrument performance.

10.7.1 High recoveries may be due to a coeluting matrix interference or the presence of high molecular weight contaminants; examine the sample chromatograph.

10.7.2 High recoveries may also be due to memory effects caused by poor sample volatility, backflash or carryover. Check instrument conditions, injection volume and injector temperature.

10.7.3 Low recoveries may be due to adsorption by the same matrix.

10.7.4 Low recoveries may also be caused by incorrect integration. The chromatographic profile of motor oils does not give baseline resolution of all components, resulting in a characteristic rise in baseline underneath the resolved hydrocarbon components known as the "unresolved complex mixture", or UCM. Do not use peak to peak integration, use forced baseline integration.

10.7.5 If the surrogate recovery is outside of established limits, the results must be flagged and an explanation offered.

10.8 Blind Quality Control check samples shall be analyzed at least twice annually.

10.9 Equipment blanks and field collected duplicates (if required) shall be analyzed with the associated sample set.

11. Method Performance

11.1 Method performance data for this study was generated by an interlaboratory study with 13 participating laboratories. The groundwater

and soil samples were supplied by an independent vendor and were spiked with a mixture of diesel, fuel oil and a fatty acid interferent.

Matrix	Spike Level	# of Labs w/ * Accept. Results	# Points	Mean % Recvy	Stnd Dev.
Water	17.7 mg/L	9	25	66.3	20.5
	132 mg/L	9	26	75.2	36.3
Soil (sonication)	35.2 mg/kg	7	16	163	90.5
	1080 mg/kg	8	23	113	46.1
Soil (soxhlet)	35.2 mg/kg	7	18	173	114
	1080 mg/kg	8	21	98.5	46.5

* Data acceptability was dependent upon the use of the correct integration techniques and/or the Grubbs test for outliers.

11.2 In a single laboratory study, known concentrations of diesel and motor oil standards were injected and the responses were calculated by this method:

Diesel in Water:	99%	Diesel in Solids	106%
10W40 in Water:	78%	10W40 in Solids:	101%

11.3 Method Acceptance Criteria - See Table 2.

12. References

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2. "DEP Manual for Preparing Quality Assurance Plans", DEP QA-001/90, September 30, 1992, Florida Department of Environmental Protection Quality Assurance Section.

3. "Method QA-2: Extractable Petroleum in Products" Revision January 10, 1990; University Hygienic Laboratory, Iowa City, Iowa.

4. "Method for Determination of Extractable Petroleum Hydrocarbons (EPH) in Soil and Water" - Draft - February 28, 1990; prepared for Total Petroleum Hydrocarbons Method Committee by Midwest Research Institute.

5. Zills, K., M. McDevitt, and J. Parr; "A Reliable Technique for Measuring Petroleum Hydrocarbons in the Environment ," presented at the conference

on Petroleum Hydrocarbons and Organic Chemicals in Groundwater, NWWA, Houston, Texas, November 1988.

6. "Leaking Underground Fuel Tank (LUFT) Field Manual," State Water Resources Control Board, State of California, Sacramento, CA Many 1988.

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8. Senn, R.B., and M.S. Johnson, "Interpretation of Gas Chromatographic Data in Subsurface Hydrocarbon Investigations," Ground Water Monitoring Review, 1987.

9. Hughes, B.M., D.E. McKenzie, C.K. Trang, L.S.R. Minor, "Examples of the Use of an Advanced Mass Spectrometric Data Processing Environment for the Determination of Sources of Wastes" presented at 5th Annual Waste Testing and Quality Assurance Symposium, July 24-28, 1989.

10. ASTM "Standard Methods for Comparison of Waterborne Petroleum Oils by Gas Chromatography," 3328-78.

11. "Measurement of Petroleum Hydrocarbons: Report on Activities to Develop a Manual", EPA UST Work Group, November 1990.

12. "Method for Determination of Residual Range Organics", AK103.0, Revision 2, May 1994 (Draft), State of Alaska, Department of Environmental Conservation.

13. "Method for Determining Diesel Range Organics", Modified DRO, PUBL-SW-141, Revision 6, July 1993, Wisconsin DNR.

Table 1

Components in Petroleum Hydrocarbon Standard

Octane ($C_{8)}$

Decane (C_{10})

Dodecane (C_{12})

Tetradecane (C_{14})

Hexadecane (C_{16})

Octadecane (C_{18})

Eicosane (C_{20})

Docosane (C_{22})

Tetracosane (C_{24})

Hexacosane (C_{26})

Octacosane (C_{28})

Triacontane (C_{30})

Dotriacontane (C_{32})

Tetratriacontane (C_{34})

Hexatriacontane (C_{36})

Octatriacontane (C_{38})

Tetracontane (C_{40})

Table 2

Method Acceptance Criteria

		% Recovery			Precision (%RSD)		
		Water	Soil		Water	Soil	
			Soxhlet	Sonication		Soxhlet	Sonication
Samples		41-101	41-224	62-204	0-20	0-25	0-25
Laboratory Control Samples		55-118	63-135	63-153	0-20	0-25	0-25
Surrogates:	OTP	82-142	57-115	62-109			
	C_{39}	42-193	61-153	60-118			

Figure 1

Example of Forced Baseline-Baseline Integration
Use to Quantitate all Samples

Figure 2

Example of Forced Baseline-Baseline Integration
Use to Quantitate all Samples

Figure 3

Example of Valley-Valley Integration of Single Peaks
Use to Quantitate Surrogate Standards Only

DO NOT USE THIS METHOD TO QUANTITATE TOTAL PETROLEUM CONCENTRATION IN SAMPLES