METHOD FOR DETERMINATION OF EXTRACTABLE PETROLEUM HYDROCARBONS BY GC/FID

1. Scope and Application

1.1 Analytes

1.1.1 This method is designed to measure the concentration of Extractable Petroleum Hydrocarbons in water and soil. This corresponds to an alkane range of C_{12}-C_{40}.

1.1.2 The method is designed to measure mid to late-range petroleum products, such as diesel and spent motor oil, where contamination extends beyond diesel range organics. If, based on a review of the chromatogram, the presence of these product types is suspected, additional efforts may be performed including but not limited to, analysis of additional reference materials. These additional efforts are not contained within this method.

1.2 Quantitation Limits

1.2.1 Quantitation limits are based on 100 ug/ml of diesel/and or motor oil in the extract and are 0.10 mg/L for waters and 4.0 mg/kg for soils.

1.3 Dynamic Range

1.3.1 Dilutions should be performed as necessary to put the chromatographic envelope within the linear range of method. This is approximately equivalent to 100 ug/mL to 5000 ug/mL of oil in the final extract.

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 25 grams of soil is spiked with a surrogate compound and extracted with methylene chloride. The extract is dried and concentrated to a volume of 1.0 mL. An (optional) internal standard is added to each extract, and 2 uL of extract is injected into a capillary column gas chromatograph equipped with a flame ionization detector (FID). Quantitation is performed by comparing the total chromatographic area to the response of oil/diesel.

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 (2) and work by the EPA Total Petroleum Hydrocarbons Methods Committee (3).

3. Definitions

3.1 Extractable Petroleum Hydrocarbons (EPH): All chromatographic peaks eluting in the same retention time window as a representative diesel/oil standard mix.

3.2 Diesel/Oil Standard mix: An aliquot of commercial motor oil (10W30) obtained from a local outlet mixed 1 to 1 with an aliquot of diesel fuel(fuel oil #2) also obtained from a local outlet.

3.3 Surrogate Control Sample: A reagent water or method blank sample spiked with the surrogate compound used in the method. The surrogate recovery is used as a laboratory control. See 7.4.2.

3.4 Laboratory Control Sample: A reagent water or method blank sample spiked with diesel fuel (fuel oil #2) as a quality control check. The spike recovery is used as a laboratory control and must be greater than 50%. See 7.4.5.

3.5 Other terms are as defined in SW-846.

4. Interferences

4.1 Other organic compounds; including chlorinated hydrocarbons, phenols and phthalate esters are measureable. As defined in the method, the EPH results include these compounds.

4.2 Method interferences are reduced by washing all glassware with with hot soapy water and then rinsing it with tap water, methanol, and methylene chloride. Reagent blanks must be analyzed with each batch or for every 20 samples to demonstrate that the samples are free from method interferences.

4.3 High purity reagents, such as Burdick and Jackson GC[2] methylene chloride or Baker capillary grade methylene chloride, must be used to minimize interference problems.

4.4 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 cross-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

6.1.1 All specifications are suggested only.

6.1.2 4 oz. amber glass wide mouth jars.

6.1.3 Separatory funnel - 2000 mL with Teflon stopcock.

6.1.4 Concentrator tube. Kuderna-Danish - 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.

6.1.5 Evaporative flask, Kuderna-Danish - 500 mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs.

6.1.6 Snyder column, Kuderna-Danish - three ball macro (Kontes K-503000-0121 or equivalent). Rotary evaporation set-up may also be used alternatively.

6.1.7 Vials - Amber glass, 10 to 15 mL capacity, with Teflon-lined screwcap. One mL glass vials with teflon-lined cap.

6.1.8 Reaction flask - Pyrex glass, 15 to 25 mL round bottom flask with standard tapered joint, fitted with a water cooled condenser and U-shaped drying tube containing granular calcium chloride.

6.1.9 Disposable pipets: Pasteur

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

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

6.4 Water bath - Heated with concentric ring cover, capable of temperature control (+/-2oC). The bath should be used in a hood.

6.5 An analytical balance capable of accurately weighing 0.0001g 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 gas 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: 12M x 0.2mm ID x 0.33 micron film thickness DB-1, or equivalent.

6.6.2.2 Other columns may be used - capillary columns are required. See 9.2.2 for GC criteria.

6.7 Sonication

6.7.1 Ultrasonic cell disrupter: A horn-type sonicator equipped with a titanium tip should be used. A Heat Systems 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 432 13 or equivalent).

6.8 Soxhlet extraction apparatus is described in Method 3540.

6.9 Nitrogen evaporator with high purity nitrogen gas source.

7. Reagents and Standards

7.1 Reagent water: Carbon filtered deionized water

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

7.3 Sodium sulfate - (ACS) granular, anhydrous. Purify by heating at 400° C for 4 hours in a shallow tray.

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

7.4.1 Optional Stock Internal Standard: 1000 ug/mL 5 a -androstane.

7.4.2 Recommended Surrogate Standard: 2000 ug/mL ortho-terphenyl (OTP). A working solution is made at 20 ug/mL in acetone (a water soluble solvent). Other appropriate surrogates may be used.

7.4.3 Diesel/Oil Standard: 1 to 1 Commercial diesel/motor oil mix at approximately 100 ng/uL up to 5,000 ng/uL.

7.4.4 Stock Laboratory Control Sample - 5000 ug/mL diesel. A working solution is made at 1000 ug/ml in methylene chloride.

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

8.1 Water samples are collected in an one liter glass container, acid preserved and soils in a glass jar. The samples are stored at 4° C from the time of collection until extraction. Extraction must be performed on waters within seven days and soils within 14 days. All analysis must take place within 40 days.

9. Procedure

9.1 Sample preparation

9.1.1 Waters are extracted according to SW-846 Method 3510 (Separatory Funnel Liquid-Liquid Extraction) or Method 3520 (Continuous Liquid-Liquid Extraction). Soil samples are extracted using Method 3550 (Sonication). Method 3540 (Soxhlet Extraction) may also be used.

9.1.2 Water extraction - Separatory Funnel

9.1.2.1 Measure a 1-L portion of the sample and transfer to the 2-L separatory funnel. If the sample is in a 1 liter or smaller bottle, mark the water meniscus on the side of the sample bottle for later determination of the sample volume. If the sample is in a larger bottle, use a 1 liter graduated cylinder. Pour the sample into a 2 liter separatory

funnel. For blanks and quality control standards, pour 1 liter of carbon filtered water into the separatory funnel.

9.1.2.2 Check and note the initial pH.

9.1.2.3 Add 1 mL of ortho-terphenyl surrogate standard at 20 ug/mL.

9.1.2.4 For every batch or 20 samples extracted, prepare duplicate laboratory control samples by adding 1 mL of 1000 ug/mL diesel (laboratory control standard) to each of two blank matrices. Daily or for every 20 samples, prepare a blank/surrogate control standard using 1 L of carbon filtered water.

9.1.2.5 For samples that were mixed before extraction, add 60 mL CH_2Cl_2 to the sample bottle to rinse the inner walls. Do **NOT** cap and shake the bottle, rinse the glass only; 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 layers to separate. If there is an emulsion, break it. If the emulsion cannot be broken (recovery of <80% of the methylene chloride, corrected for water solubility of methylene chloride), transfer the sample, solvent, and emulsion into the extraction chamber of a continuous extractor and proceed as described in 9.1.3.

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

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 beaker described in 9.1.2.7. Record the volume recovered.

9.1.2.9 Put a plug of glass wool in a funnel and fill about 2/3 full 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 Kuderna-Danish (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.

9.1.2.10 Add a boiling chip to the K-D and attach a 3 ball Snyder 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.

9.1.2.11 Place the K-D in a heated water bath set at 95° C so that the receiver tube is immersed in hot water and the entire lower rounded surface is bathed in steam. At a proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume reaches 5-10 mL, remove the K-D from the bath and allow it to cool completely.

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

9.1.2.13 After the K-D has cooled, rinse the Snyder column and middle flask with a small amount of CH_2Cl_2. Transfer the extract to a calibrated 15 mL centrifuge tube, rinsing 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.

9.1.2.14 Carefully concentrate the extract to 1.0 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.

9.1.2.15 Record the prep information for the extraction and concentration steps. The sample extract is ready for analysis (See Section 9.2 through 9.6).

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 and 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 For samples in 1 liter of smaller bottles, mark the meniscus on the side of the sample bottle and pour approximately 1 liter of the sample into the extractor flask. Measure the exact volume by adding tap water to the bottle to the marked level and measuring the volume with a graduated cylinder. For samples in bottles larger than 1 liter, measure 1 liter of the sample in a graduated cylinder. Record the volume.

9.1.3.6 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. Record the total volume carbon filtered water that was added on the prep sheet.

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

9.1.3.8 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.

9.1.3.9 Check all extractor joints for leaks with a Kimwipe. Allow the extraction to proceed for 18-24 hours.

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

9.1.3.11 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.

9.1.3.12 Go to 9.1.2.9 and proceed with the prep.

9.1.4 Soil preparation - Sonication

9.1.4.1 Remove large rocks or other foreign materials and mix the sample well. Chop any vegetation into small pieces.

9.1.4.2 Weigh 25 g of the original sample into a 250 mL centrifuge bottle. Add 25 g of dried Na_2SO_4 and stir the mixture well with a steel spatula. The sample should have a grainy texture - if it forms a large clump, add more Na_2SO_4 and note it on the prep sheet.

9.1.4.3 Add 100 mL of CH_2Cl_2 to all samples.

9.1.4.4 Add 1 mL of 20 ug/mL ortho-terphenyl to all samples and standards. Mix the samples immediately.

9.1.4.5 Add 1 mL of 1000 ug/mL diesel (laboratory control standard) to the duplicate laboratory control standards. These standards should contain 25 g of Ottawa Sand. In addition, prepare a reagent blank/surrogate control standard containing 1 mL of 20 ug/mL ortho-terphenyl.

9.1.4.6 Sonicate the samples for 1.5 minutes at an output setting of 10 with the 3/4 inch sonicator horn 1/2 inch below the surface of the solvent. The sonicator should be in the 1 second pulse mode, with the duty cycle set at 50%. Centrifuge the samples for 3-5 minutes at 35 RPM.

9.1.4.7 Decant the solvent layer into a rinsed 400 mL beaker.

9.1.4.8 Repeat the extraction twice more using 100 mL aliquots of CH_2Cl_2 each time. Collect these extracts in the same beaker described in 9.1.4.9.

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

9.1.4.10 Go to 9.1.2.9 and proceed with the prep.

9.1.5 Dilution Technique

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

9.1.5.2 Weigh 1 g of sample into a 10 mL volumetric flask. Dilute to 10 mL with CH_2Cl_2. Store in a 12 mL vial.

9.2 Gas Chromatography

9.2.1 Conditions (Recommended): Set helium column flow to 1 mL/min. Set column temperature to 35° C for 14 minutes, then 10° C/min to 210° C , then raise to 320° C at 40/min and hold 10 min. The FID temperature should be set at 300° C and the injector to 250° C. These conditions may vary depending upon equipment.

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

9.2.2.1 Resolution from the solvent front and o-terphenyl of C_{22}.

9.2.2.2 The column must be capable of separating typical oil components from the surrogate and internal standards.

9.3 Calibration

9.3.1 Calibrate the GC with an initial five point calibration using the commercial diesel/oil standard (7.4.4). Tabulate the area response of the diesel/oil standard. The ratio of the response to the amount injected, defined as the response factor (RF), can be calculated for the standard at each concentration. If the percent relative standard deviation (%RSD) is less than 25% over the working range, linearity through the origin can be assumed, and the continuing calibration response factor can be used in place of a calibration curve.

Response Factor = Total area of commercial diesel/oil x I.S. amount (mg/mL) / Total diesel/oil standard amount (mg/mL) x I.S. area

Note: I.S. = Internal Standard (optional)

Alternately, external standard calibration may be used (See SW-846 Method 8000).

9.3.2 The working response factor or calibration curve must be verified on each working day by the injection of a continuing calibration standard (CCS), mid-point. If the response for this standard varies from the predicted response by more than +/-25%, a new calibration curve must be prepared.

Percent Difference = $R_1 - R_2 / R_{avg} \times 100$

where: R_1 = Average RF from the calibration curve

R_2 = Response Factor from CCS

$R_{avg} = (R_1 + R_2)/2$

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 injection 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 three absolute retention times for the surrogate and/or internal standard.

9.4.2.1 The retention time window for individual peaks is defined as 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 each standard 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 2 uL using the conditions established in 9.2.

9.5.2 For internal standard calibration, 5-a androstane internal standard is spiked into each sample and standard at a concentration of 20 ug/mL of sample extract. 20 uL of 5-a

Androstane stock at 1000 ug/mL may be spiked into the 1 mL final volume or a corresponding amount may be added to an aliquot of the final extract.

9.5.3 If initial calibration (9.3.1) has been performed, verify the calibration by analysis of a mid-point CCS (9.3.2). The midpoint standard must also be run once every ten runs and at the end of each sequence.

9.5.4 Calculate the percent difference of the response factor from the mean response factor as in 9.3.2. If the response factors have a percent difference >+/-25%, the instrument must be recalibrated (9.3.1).

9.5.5 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 generated by projecting a horizontal baseline between the retention times observed for C_{12} and C_{40}. This area is subtracted from the EPH area generated in the same manner for the samples.

Methylene chloride blanks should also be run after samples suspected of being highly concentrated to prevent carryover.

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

9.6 Calculations

9.6.1 Internal Standard Calibration: The concentration of Extractable Petroleum Hydrocarbons in the sample is determined by calculating the absolute weight of analyte chromatographic peaks eluting in the defined retention time window of oil, using the calibration curve or the response factor determined in 9.3.2. Refer to 9.4. The concentration of Extractable Petroleum Hydrocarbons is calculated as follows:

Aqueous/Soil samples:

$C_s = (A_x / A_s) \times (C_{is} / RF) \times (V_t / V_s) \times D$

Where:

C_s = Concentration of Extractable Petroleum Hydrocarbons (mg/L or mg/kg).

A_x = Response for the Extractable Petroleum Hydrocarbons in the sample, units in area.

RF = Response Factor from continuing calibration (See 9.3.1).

A_s = Response for the internal standard, units same as for A_x.

C_{is}= Concentration of Internal Standard (mg/mL).

V_t = Volume of Final extract (mL).

D = Dilution factor

V_s = Volume of sample extracted in L or kg.

9.6.2 Alternately, external standard calibration may be used (See SW-846 Method 8000).

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 as outlined in Method 8000, Section 8.0.

10.2 The laboratory must, on an ongoing basis, demonstrate through the analysis of quality control check standards that the operation of the measurement system is in control.

10.3 After successful calibration (Section 9.3), analyze a Surrogate Control Sample. This standard is also the reagent blank sample and is analyzed with every analytical batch or sequence. The surrogate recovery should be within established limits (Table 1) and the sample should not have Extractable Petroleum Hydrocarbons above the practical quantitation limit.

10.4 Every batch or 20 samples, duplicate Laboratory Control samples must be analyzed. The accuracy and precision of the duplicate standards must be within established limits (Table 1).

10.5 Each laboratory should generate control limits based on the average recovery +/-3 standard deviations.

10.6 If any of the criteria in 10.3 and 10.4 are not met, the problem must be corrected before samples are analyzed.

10.7 Calculate the surrogate standard recovery in each sample. If recoveries are outside established limits, verify calculations, dilutions and standard solutions. Verify instrument performance.

10.7.1 High recoveries may be due to a coeluting matrix interference; examine the sample chromatogram.

10.7.2 Low recoveries may be due to the sample matrix.

10.8 Field blanks, duplicates and matrix spikes are recommended for specific sampling programs. Matrix spikes should use the spike levels specified for laboratory control samples.

11. References

1. USEPA "SW-846 Test Methods for Evaluating Solid Waste", 3rd Edition; Methods 8000, 8100, 3510, 3520, 3540, and 3550.

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

3. "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.

4. Zillis, 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.

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

6. Fitzgerald, John "Onsite Analytical Screening of Gasoline Contaminated Media Using a Jar Headspace Procedure" in Petroleum Contaminated Soils, Vol. 2, 1989.

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

8. 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.

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

TABLE I
ACCEPTANCE CRITERIA FOR LCS AND SCS

Laboratory Control Sample	**%Rec**	**Relative %Difference**
Extractable Petroleum Hydrocarbons	50-100	20
Surrogate Control Standard		
ortho-Terphenyl	50-150	