

NWTPH-HCID

Hydrocarbon Identification Method for Soil and Water

Summary

This method is a qualitative and semi-quantitative procedure. It is used for groundwater or surface water, and soil/sediment from sites where the petroleum products are unknown and/or when multiple types of petroleum products are suspected to be present. This method is used to identify petroleum products containing components from C7 to C30 range, as well as heavy oils, with specific product confirmation by pattern matching ("fingerprinting") employing capillary gas chromatography with flame ionization detection (GC/FID). EPA method 3510 has been adapted as the extraction procedure for the water portion of this method.

While this method is intended to be primarily qualitative, it can be used to eliminate the need for further analyses for those samples which demonstrate TPH levels significantly below the regulatory limits. If the sample contains toluene to dodecane (gasoline range), dodecane through tetradecane (diesel range) and/or an unresolved chromatographic envelope greater than tetradecane (e.g. motor oils) above the reporting limits of this method, then the final quantitation must be performed by methods specific for these mixtures. Since the water extraction procedure in this method is identical to that found in the water portion of NWTPH-Dx (semi-volatile petroleum products, i.e. from kerosene through heavy fuel oils), these products may be quantitated using this extract. Because of the possible loss of volatile compounds in the extraction and concentrations steps, gasoline, mineral spirits and other volatile petroleum products that exceed the reporting limits of this method must be quantitated using the NWTPH-Gx method.

The reporting limits for water are 0.25 mg/L for gasoline, 0.63 mg/L for #2 diesel and motor oils. The reporting limits for soil/sediment are 20 mg/Kg for gasoline, 50 mg/Kg for #2 diesel, and 100 mg/Kg for motor oil, all reported on a dry weight basis. These values for soil/sediment assumes 100% solids and will be higher depending on the actual moisture content.

The method relies heavily upon the experience of the analyst for the identification of the specific petroleum product(s) that may be present. Therefore, this method must be run by, or under the direct supervision of, analysts experienced in the use of GC and in the interpretation of gas chromatograms of both fresh and weathered petroleum products.

Equipment and Reagents

Gas Chromatograph, w/wo autosampler

Capillary split/splitless injector

Flame ionization detector

Suggested Capillary Column:

J&W DB-1 or DB-5, 30 M x 0.25 mm or 0.32 mm with 0.25 um film thickness capillary column or equivalent

Chromatography Data System

VOA Vial: 40 mL glass vial with Teflon coated cap septum, Eagle Picher or equivalent

Syringe: Hamilton #701, 10 uL or equivalent

Ultrasonic Bath

Glass Wool: Pyrex or equivalent

Centrifuge tubes: 5 mL or 15 mL, calibrated in 0.1 mL increments

Analytical Balance: accurate to at least 0.0001 g

Volumetric Flasks: 10 mL, ground glass with ground glass stopper

Separatory funnels: 500 mL, Teflon stopcocks

Kuderna-Danish (KD) Flasks: 250 mL or equivalent

Snyder Columns: 3-ball, 24/40 ground glass joint

Concentrator Tubes: 10 mL

Methylene Chloride: Burdick and Jackson Brand or equivalent

N-Evap Concentrator or equivalent

Standards

Retention Time Standards. Prepare a composite standard, using methylene chloride as the solvent, consisting of toluene, dodecane and tetracosane at 25 ug/mL each. Additional compounds may be added at the discretion of the analyst. The use of this standard is to establish the retention time windows for the quantitation of gasoline #2 diesel and motor oils.

Reference Standards. Prepare individual petroleum product reference standards (i.e. gasoline, mineral spirits, kerosene and #2 diesel oil), using methylene chloride as the solvent, at approximately 50 ug/mL. Prepare a non-synthetic motor oil (pennzoil SAE 30 or equivalent) reference standard at 200 ug/mL. The preparation of reference standards for other types of petroleum products is recommended. The use of these reference standards is to insure the accurate identification of petroleum product contamination by chromatographic pattern matching ("fingerprinting") and establish retention time windows for those petroleum products not determined with the individual compound retention time standard.

Gasoline Stock Standard. A stock standard is prepared by placing approximately 9 mL of methylene chloride in a 10 mL volumetric flask. Tare the flask/methylene chloride and add about five drops of

non-oxygenated regular unleaded gasoline, assuring that the liquid falls directly into the methylene chloride without contacting the neck of the flask. Reweigh the flask and dilute to volume with methylene chloride, stopper and mix by inverting the flask several times. It is important that the analyst minimize the amount of time that the flask is left unstoppered, to reduce the loss of gasoline through volatilization. The use of a commercially prepared gasoline standards is acceptable if it is certified as non-oxygenated gasoline or if the gasoline concentration has been adjusted to reflect the contribution of the oxygenate. Calculate the gasoline concentration as follows:

$$\text{Stock, ug / mL} = \frac{(\text{final wt, mg}) - (\text{tare wt, mg})}{10 \text{ mL}} \times \frac{1000 \text{ ug}}{\text{mg}}$$

Note: The use of oxygenated regular unleaded gasoline for the gasoline stock standard is allowed if the weight (mass) of the gasoline used is adjusted for the weight (mass) contribution of the oxygenate to the gasoline. This will necessitate the analysis of the gasoline for the specific oxygenate(s) present to determine the concentration. The analysis for the oxygenates will be conducted by either of the methods published in the Federal Register - Appendix B and C - Testing Procedures - Vol. 57, No. 24, Wednesday, February 5, 1992, Notices. Alternate methods for the analysis of gasoline oxygenates must be approved by the Oregon's Department of Environmental Quality and/or Washington's Department of Ecology prior to use.

Diesel Stock Standard. A stock standard is prepared by adding about five drops of #2 diesel oil stock to tared 10 mL volumetric flask. Reweigh the flask and bring it to volume with methylene chloride, stopper and mix by inverting the flask several times. Calculate the concentration of this standard in the same manner as the gasoline stock standard. The use of a commercially prepared #2 diesel standard is an acceptable alternative to the above procedure.

Motor Oil Stock Standard. A stock standard is prepared by adding about ten drops of a non-synthetic SAE 30 weight motor oil (Pennzoil or equivalent) to a tared 10 mL volumetric flask. Reweigh the flask, bring it to volume with methylene chloride, stopper and mix by inverting the flask several times. Calculate the concentration of this standard in the same manner as the gasoline stock standard. The use of commercially prepared motor oil standards is an acceptable alternative to the above procedure.

Note: The Diesel and Motor Oil Stock Standards required in this method are identical to those required for NWTPH-Dx (extended diesel method including all semi-volatile petroleum products eluting after gasoline, e.g. kerosene, diesels, mineral oils, lubricating oils, heavy fuel oils, etc.).

Surrogate Stock Standard. Suggested surrogates for use in this method are bromofluorobenzene and pentacosane. The use of different or additional surrogates is optional. Prepare the surrogate stock standard by weighing 50 mg of each surrogate compound into a 10 mL volumetric flask, then bring to volume with methylene chloride for a final concentration of 5000 ug/mL for each surrogate compound. The use of a commercially prepared surrogate solution(s) is an acceptable alternative to the above procedure.

Composite Calibration Working Standard. Using serial dilutions of the stock standards, prepare a mixture for water analyses that contains 10 ug/mL of gasoline, 25 ug/mL of #2 diesel oil and the surrogate standard. For soil/sediment analyses this standard should be prepared to contain 20 ug/mL of gasoline, 50 ug/mL of #2 diesel and the surrogate standard. Add the appropriate volumes, using the equations listed below, and adjusting for the concentration change created by any serial dilutions, of gasoline stock standard, #2 diesel stock standard and the surrogate stock standard to a 10 mL volumetric flask, then dilute to volume with methylene chloride. Stopper and mix by inverting the flask several times. The surrogate standard should be added to a level sufficient to produce a surrogate concentration of between 5 and 50 ug/mL.

$$\text{Volume Gasoline Stock, } \mu\text{L} = \frac{20 (\text{soil}) / 10 (\text{water}) \text{ ug} / \text{mL} \times 10 \text{ mL}}{\text{Gasoline Stock Conc, ug} / \text{mL}} \times \frac{1000 \text{ } \mu\text{L}}{\text{mL}}$$

$$\text{Volume Diesel Stock, } \mu\text{L} = \frac{50 (\text{soil}) / 25 (\text{water}) \text{ ug} / \text{mL} \times 10 \text{ mL}}{\text{Diesel Stock Conc, ug} / \text{mL}} \times \frac{1000 \text{ } \mu\text{L}}{\text{mL}}$$

This mixture corresponds to 0.25 mg/L gasoline and 0.63 mg/L #2 diesel oil for water and 20 mg/Kg gasoline and 50 mg/Kg diesel in soil following the extraction and analytical procedures of this method.

The motor oil calibration working standard should be made at a concentration of 250 ug/mL for water and 100 ug/mL for soil following the procedure outlined above. This will correspond to a reporting value of 0.63 mg/L for water and 100 mg/kg for soil. If, in the opinion of the analyst, the GC sensitivity to 100 ug/mL of motor oil is insufficient, the analyst is allowed to increase the concentration of this standard and to concentrate a portion of the extract to achieve the reporting limit for soil.

Surrogate Working Standard. Prepare a surrogate working (spiking) standard, using the procedure outlined above, that will yield between 5 ug and 50 ug/mL of the surrogate compounds in the 10 mL sample extract produced in this method.

Note: All samples must be collected in glass jars with Teflon lined lids (Eagle Picher or equivalent) and held at 4 degrees C until extracted. A volume of 400 mL is the minimum sample size to achieve the reporting limits as stated, however, larger volumes are allowed as long as the solvent/sample ratio is maintained. Samples must be extracted within 7 days (for water) or 14 days (for soil/sediment) of the date of collection. The preservation of water samples in the field, to a pH of less than 2 with 1+1 HCL, is recommended.

Extraction Procedures

Water Samples

Mark the water meniscus on the sample jar for later volume determination. Pour the sample into a 500 mL separatory funnel, add the surrogate solution (to achieve the desired concentration in a 10 mL extract). Add 30 mL of methylene chloride to the sample jar, cap and shake the jar vigorously for a few seconds to wash off any hydrocarbons adhering to the side of the jar. Add this solvent to the separatory funnel, stopper and shake vigorously, venting frequently, for one minute. Allow the two phases to separate, then drain the solvent into a 250 mL K-D flask fitted with a 10 mL concentrator tube. Repeat the extraction twice more using 30 mL of methylene chloride, each time, adding the solvent to the K-D.

Attach a 3-ball Snyder column to the K-D and concentrate the sample extract to 5 - 10 mL on a stream bath. Remove the K-D apparatus and allow it to cool prior to disassembly. During disassembly, rinse the Snyder/K-D joint and K-D/concentrator joint with approximately 1 mL of methylene chloride and add these rinsings to the extract. Adjust the volume of the extract to 10 mL. For those samples which exceed 10 mL, place the concentrator tube into an N-Evap and, under a gentle stream of nitrogen, reduce the volume to 10 mL. Transfer 1 mL of the extract (to be used for the gasoline or gasoline/diesel determination) to an autosampler vial fitted with a screw top and a Teflon coated septum. Concentrate the remainder of the extract (to be used for heavy oils determination) to 0.9 mL, transfer it to a 2 mL autosampler vial equipped with a screw top and a Teflon coated septum. Store both vials in a refrigerator until analysis.

Each extraction set must include one method blank (organic-free water of similar volume to the samples) per 20 samples. The method blank is to receive the surrogate solution and to be extracted and analyzed in the same manner as the samples.

EPA method 3520, Continuous Liquid-Liquid Extraction, may be substituted as an alternate extraction procedure to that outlined above.

Soil Samples

Weigh approximately 10 grams of soil into a 40 mL VOA vial and record the weight to the nearest 0.001 grams. Add 5 grams of anhydrous sodium sulfate, surrogate working solution and 10 mL of methylene chloride to the VOA vial. Cap the vial and place it (no more than 5 at a time) in a sonic bath for 5 minutes. Shake the vials well and return them to the sonic bath for 5 more minutes. A minimum of one method blank per extraction set or 20 samples, whichever is more frequent, must be prepared along with the samples. One sample duplicate must also be extracted for samples set from one to ten samples and two duplicates for sets from eleven to twenty samples.

Determine the moisture content of the samples, for use in the final calculations, by the following procedure. Immediately after weighing the sample for extraction, weigh 5-10 grams of the sample into a tared crucible. Dry the sample/crucible overnight at 105 °C. Reweigh the sample/crucible after allowing it to cool to room temperature. Calculate the % solids as follows: $[(\text{grams of dry sample} / \text{grams of wet sample}) \times 100]$.

If the extract contains significant moisture, elute the solvent phase through an anhydrous sodium sulfate micro-column. Place a portion of the extract in a 2 mL autosampler vial (screw cap, Teflon coated septum), taking care to minimize the volume of headspace, and store the vial in a refrigerator until analyzed. Concentration of the extract, when necessary, will be conducted using an N-Evap with a gentle stream of nitrogen. This concentrate should be stored in the same manner as noted above.

Note: Anhydrous sodium sulfate micro-columns are prepared by plugging a 5 3/4" length disposable Pasteur pipette (pre-rinsed with methylene chloride) with glass wool (precleaned with methylene

chloride) and adding approximately 3 cm of anhydrous sodium sulfate (previously muffled at 430 °C overnight in a shallow pan and stored in a glass jar with a Teflon lid liner).

For samples containing petroleum products other than gasoline, diesel, or motor oil, the analyst must either prepare calibration standards of them by the methods listed above or analyze the sample by the fully quantitative method, e.g. NWTPH-Gx. Other calibration standards produced for use in this method must be at an equivalent concentration to the previously established standards, e.g. mineral spirits at the gasoline concentration, kerosene at the diesel concentration.

As more information becomes available on new extraction techniques, the Washington State Dept. of Ecology's Manchester Laboratory and Oregon's Department of Environmental Quality will publish descriptions of acceptable alternate extraction methods.

Suggested GC Parameters

Sample injection Volume = 2 uL

Injector Temperature = 290 °C

Detector Temperature = 300 °C

Hydrogen Flow = 25-35 mL/min

Air Flow = 300-400 mL/min

Make-up Gas Flow = 30 mL/min

GC Temperature Program = Initial temperature of 50 °C and hold for 2 minutes; ramp the temperature 10 °C /min to 320 °C and hold for 5 minutes.

Product Identification

Petroleum products are to be identified by pattern matching with reference product chromatograms generated the same day as the sample analysis. The term "gasoline range" or "diesel range" hydrocarbons, or derivations of them, should only be used when the analyst is unable to identify the petroleum product present. When these terms are used, it is to indicate the presence of compounds eluting from toluene to dodecane, for the former term, and from dodecane through tetracosane, for the latter term. Motor oils, hydraulic fluids and similar petroleum products which present an unresolved chromatographic envelope of compounds, originating or extending beyond tetracosane, may be reported using the collective term, lube oil, unless specific identification is possible. Heavy fuel oils, e.g. fuel oil #6 or Bunker C, which contain a diesel range component as well as a lube oil (and higher) range may be reported using the collective term, heavy fuel oil, unless specific identification is possible. These products should not, however, be confused with mixtures of #2 diesel and motor oils.

Note: The actual identification of the grade or type of lube oil and heavy fuel oil may require equipment and techniques beyond the scope of this method.

Analysis Procedure

The analysis is accomplished by injecting 2 uL of the 10 mL extract, either manually or by autosampler, into the GC using the splitless injection mode. The results from this injection are, for quantitation purposes, compared directly against the single point calibration standard for the product(s) identified. The injection of 2 uL of the concentrated extract (1 mL equivalent) is used primarily for heavy oil determination, because of the reduced sensitivity of the FID to late eluting

motor oil-like products. It may be used for the determination of #2 diesel oil and other diesel range petroleum products but it may not be used for the determination of gasoline or gasoline range petroleum products because of the potential for loss of the more volatile components during the concentration step.

Calculations

Gasoline. The area of the components, toluene to dodecane of the calibration standard, is integrated to the baseline as a group. The samples and method blanks are integrated in the same manner and the group areas are compared. If the sample area exceeds the calibration standard area, proceed with method NWTPH-Gx for accurate quantitation using a fresh aliquot of the sample.

If the sample area does not exceed the calibration standard area, then report the gasoline concentration as less than 0.25 mg/L for water or 20 mg/kg for soil. This soil value for gasoline, and the subsequent petroleum products, assumes 100% solids and will be higher depending on the actual moisture content.

Other volatile petroleum products, identified as being present (e.g. mineral spirits), must be compared to the appropriate standard produced at the same concentration as gasoline. The requirement for further analyses is determined following the criteria for gasoline as noted above.

Note: For samples containing only #2 diesel oil, kerosene, etc., the portion of these products, that elute within the retention time range of gasoline, should not be identified and/or quantitated as gasoline or gasoline range petroleum.

Diesel. The area of the components, dodecane through tetracosane of the calibration standard, is integrated to the baseline as a group. This integration must include the unresolved envelope of compounds as well as the discrete component peaks. The sample is integrated in the same manner and the group areas are compared. If the sample area exceeds the calibration standard area, then proceed to method NWTPH-Dx. If the sample does not exceed the calibration standards area, then report the #2 diesel concentration as less than 0.63 mg/L for water or 50 mg/Kg for soil.

Other semi-volatile petroleum products, identified as being present (e.g. kerosene), must be compared to the appropriate standard produced at the same concentration as #2 diesel. The requirement for further analyses is determined following the criteria for #2 diesel as noted above.

Lube Oil. For those samples which consist primarily of only an unresolved chromatographic envelope of components eluting after tetracosane, compare their area to the area of the motor oil standard by integrating the unresolved envelope to baseline. If the sample exceeds the standard area, then proceed to method NWTPH-Dx. If the sample area is less than the standard, then report the lube oil concentration as less than 0.63 mg/L for water or 100 mg/Kg for soil. Samples identified as containing heavy fuel oil must be quantitated to the same value as lube oil by utilizing a heavy fuel oil standard and following the procedure outlined for lube oil.

Note: The analyst is expected to adjust the retention time windows used for quantitation of petroleum products, other than gasoline, #2 diesel, or motor oil/lube oils, to incorporate the majority of the chromatographable components associated with those identified products.

If, in the judgement of the analyst, the area of an identified petroleum product other than gasoline, diesel, and motor oil would exceed the reporting limit, the analyst is allowed to report a "greater than" value for that product without performing the quantitative analysis. The analyst must then proceed to the appropriate fully quantitative analytical procedure, e.g. NWTPH-Dx, for the identified petroleum product.

Quality Assurance

The addition of an appropriate extraction surrogate to samples and method blank(s) is required. The surrogate recovery for all samples and blanks should be between 50% and 150% and must be reported with the petroleum results unless the quantity of the petroleum product(s) preclude its determination. The laboratory should analyze one sample from each site in duplicate for sample sets of 10 or less and two samples in duplicate for sets of 11 to 20 samples (i.e. 10% QA). If either of the duplicate results are positive, the sample is to be considered positive. Since this method precludes the preparation of analytical duplicates, the laboratory should recommend that the project manager collect and submit field duplicates for analysis. The laboratory must analyze method blanks prepared identically to the samples. Organic free water must be used in the preparation of water method blank. No "sample" is necessary for use with soil/sediment method blanks.

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