NWTPH-Dx

Semi-Volatile Petroleum Products Method for Soil and Water

Summary

The NWTPH-Dx method is intended to replace the Oregon's Department of Environmental Quality TPH-D and Washington's Department of Ecology WTPH-D methods and to present a more comprehensive approach to semi-volatile petroleum product analyses. NWTPH-Dx adapts Oregon's TPH, Washington's WTPH and EPA SW-846 Methods 3510, 3540/3550 and 8000 and covers the quantitative and qualitative analysis of semi-volatile petroleum products, i.e. jet fuels through heavy fuel oils, in soil and water. The method involves extracting the samples with methylene chloride and injecting a portion of the extract into a gas chromatograph (GC) equipped with a flame ionization detector (FID). This method specifies criteria for the identification and quantitation of semi-volatile petroleum products. A clean-up procedure, which may be used to aid in the removal of non-petroleum based organic interferences, i.e. biogenic interferences, has been included. When the type of petroleum product is unknown, #2 diesel will initially be used as the default petroleum standard.

The reporting limits are 25 mg/kg (soil) and 0.25 mg/L (water) for the petroleum products in the elution range of jet fuels through #2 diesel. For petroleum products eluting after #2 diesel oil, e.g. motor oils, hydraulic fluids, and heavy fuel oils, the reporting limits are 100 mg/kg (soil) and 0.50 mg/L (water). All soil results are reported on a dry weight basis. Since this value assumes 100% solids and therefore will be higher depending on the actual moisture content, the analyst is permitted to concentrate the extract to obtain these reporting limits. When doubt exists as to which reporting limit is applicable for the petroleum product present, the analyst should use the lower value.

The method is applicable for the identification, by pattern matching ("fingerprinting"), and quantitation of semi-volatile petroleum products. These include kerosenes, jet fuels, diesel oils, fuel oils, lubricating oils, hydraulic fluids, mineral oils and insulating oils, e.g. transformer oils. In general, those petroleum products which do not contain a substantial volatile fraction, i.e. the majority of the components eluting outside of the gasoline range, should be analyzed by this method.

Note: The use of GC/MS (Mass Spectrometry) or GC/AED (Atomic Emission Detector) may be substituted for GC/FID as long as all other method parameters are met.

This method is to be used 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

Flame Ionization Detector

Capillary Split/Splitless Injector

Suggested Column:

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

Chromatographic Data System: Capable of group integrations

Analytical Balance, accurate to a least 0.0001 grams

Volumetric Flasks, 10 mL, ground glass stoppered

N-Evap Concentrator or equivalent

Centrifuge tubes, 10 or 15 mL, glass, calibrated in 0.1 mL increments

Centrifuge tubes, 10 or 15 mL, glass, disposable

Kaderna-Danish (K-D) Flasks, 250 mL

Concentrator Tubes, 10 mL

Snyder Columns, 3-ball, 300 mm length

Sodium Sulfate, anhydrous

Methylene Chloride, Burdick and Jackson brand, gas chromatography/pesticide residue grade or equivalent

Sulfuric acid, concentrated

Silica gel, 100/200 mesh, Baker Analyzed Reagent grade or equivalent - Before use, activate for at least 16 hours at 130 degrees C in a shallow tray

Petroleum Product Standards: Available from commercial sources

Note: All samples shall be collected in Eagle Picher, or equivalent, glass jars and held at 4 degrees C until extracted. The holding time, from the date of collection to extraction, is 14 days for soil and preserved water. For unpreserved water, the holding the holding time is 7 days. Preservation is accomplished by adjusting the pH of the water sample to approximately 2 with the addition of 1+1 HCl.

Suggested GC Parameters

Sample Extract Injection Volume = 2 uL

Injector Temperature = 290 degrees C

Detector Temperature = 300 degrees C

Hydrogen Flow = 25-35 cc/min

Air Flow = 300-400 cc/min

Helium Make-up Gas Flow = 30 cc/min

Helium Carrier Gas Head Pressure = 15 psi

GC Temperature Program:

Initial temperature = 50 degrees C, hold 2 minutes

Temperature Ramp Rate = 20 degrees C per minute

Final Temperature = 320 degrees C, hold for 10 minutes

Standards

Reference/Stock Standards: Prepare individual petroleum product reference/stock standards, e.g. kerosene, #2 diesel oil, transformer oil (mineral oil based) and Bunker-C fuel oil.

Add 5 to 10 drops of the pure petroleum product to a zero tared 10 mL flask. Record the weight and bring the flask to volume with methylene chloride, stopper and mix by inverting the flask several times. Calculate the concentration of these standards using the equation shown below. The use of commercially prepared standards is an acceptable alternative to the above procedure. Analysts may not use artificial standards, e.g. diesel range organics mixtures, etc., for quantitation purposes in place of authentic petroleum products.

These standards are to be used to produce calibration working standards which should be used to insure the proper identification of petroleum products by chromatographic pattern matching ("fingerprinting") as well as accurate quantitation.

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

Calibration Working Standards: Using the stock standards, prepare calibration working standards for the identified petroleum product(s) to be quantitated. Add the appropriate volume(s), using the equation shown below and adjusting for the concentration change created by any serial dilutions, to a 10 mL volumetric flask(s). Dilute to volume with methylene chloride. Calibration standards must, at a minimum, (1) provide a five point calibration curve, (2) include a sufficiently low standard to provide the necessary reporting limits, and (3) define the linear working range of the instrument.

In order to be acceptable, the calibration curve must have a linear correlation coefficient of at least 0.990 and none of the standards may vary from their true (known) value by more than plus/minus 15%. #2 diesel oil is the default petroleum product for reporting purposes.

Stock Surrogate Standard: Prepare the stock surrogate standard by weighing 50 mg of the surrogate compound(s) into a 10 mL volumetric flask. Bring the flask to volume with methylene chloride for a final concentration of 5000 ug/mL for the surrogate compound. The use of commercially prepared surrogate solutions is an acceptable alternative to the above procedure.

Note: The suggested surrogates are 2-fluorobiphenyl, o, or p-terphenyl or pentacosane. The use of other surrogates is optional. Selected surrogate compounds must be non-polar, unaffected by the cleanup procedure, i.e. the concentrated sulfuric acid/silica gel treatment, and lacking in significant interferences in most standard petroleum products.

Working Surrogate Spike: Using serial dilutions of the stock standard, prepare a surrogate working standard. Add the appropriate volume of the stock surrogate standard, using the equation listed below, and adjusting for any serial dilutions, to a 10 mL volumetric flask and dilute to volume with methylene chloride. Stopper and mix by inverting the flask several times. The surrogate working standard should be added to a level sufficient to produce a surrogate concentration between 5 and 50 ug/mL.

$$Volume\ Stock,\ uL\ =\ \frac{(Cal\ Std\ Conc,\ ug\ /\ mL)\ x\ 10\ mL}{Stock\ Conc,\ ug\ /\ mL}\ x\ \frac{1000\ uL}{mL}$$

Store all standards in a refrigerator until needed. Allow them to come to room temperature prior to use.

Sample Extraction

Soil Matrix

Weigh approximately 20 grams of soil, recording the weight to the nearest 0.01 grams, and approximately 20 grams of anhydrous sodium sulfate into a 150 mL beaker. Mix completely with a spatula. The mixture should have a grainy texture. If it forms a large clump, add more anhydrous sodium sulfate and grind to grainy texture. Add the appropriate volume of working surrogate standard, 50 mL of methylene chloride and sonicate for 3 minutes utilizing the horn sonicator and power settings in SW-846 Method 3550. Allow the mixture to settle then collect the extract in a 250 mL Kuderna-Danish (KD) flask to which is connected a 10 mL concentrator tube.

Repeat the extraction twice more and add these extracts to the KD. Attach a 3 ball Snyder column and concentrate the extract on a steam bath to a volume of 5-10 mL. Allow the K-D to cool to room temperature. Disassemble the K-D, rinsing the Snyder/K-D and K-D/concentrator tube joints with 1-2 mL of methylene chloride. Add these rinsings to the extract. If necessary, place the concentrator tube in an N-Evap and reduce the volume to 10 mL under a gentle stream of nitrogen. At this point, proceed to the sample cleanup procedure if applicable or transfer a portion of the extract to a 2 mL autosampler vial fitted with a screw top and a Teflon lined septum. Store the extract in a refrigerator until analyzed. If the extract is highly colored or forms a precipitate, a dilution may be necessary to stay within the calibration range. The use of the EPA method 3540 (soxhlet) in place of Method 3550 is optional.

Determine the moisture content of the samples by the following method. Immediately after weighing the sample for extraction, weigh approximately 10 grams of the sample into a tared crucible and record the weight. Dry the sample/crucible overnight at 105 degrees C. Reweigh the sample/crucible after allowing it to cool to room temperature and record the weight. Calculate the % solids as follows: [(grams of dry sample/grams of wet sample) x 100].

Along with each sample set, run at least one duplicate sample per set of 10 or fewer samples (10%) and, for each extraction day, at least one method blank (5%). Spiking of surrogates, extraction and analyses of the QC samples will be conducted identically to the regular samples with the exception that no soil is added to the method blank.

Water Matrix

Allow the sample to come to room temperature and mark the meniscus for later use in volume determination. Pour the sample into a separartory funnel and adjust the pH to approximately 2 with 1+1 HCl and add the appropriate volume of surrogate working solution. Add 30 mL of methylene chloride to the sample jar and rotate the jar at a sufficient angle to wash the walls. Pour the solvent into the separatory funnel, stopper, and shake it vigorously for one minute, venting frequently. After the two phases have separated, drain the solvent into a 250 mL K-D flask to which is attached a 10 mL concentrator tube.

Note: Due to possible loss of analytes from the water to the sample jar walls, the entire sample must be consumed in the extraction and no aliquots may be used. Since the reporting limits are

calculated on a 400 mL sample volume, sample jar size should be appropriate for this volume. For larger sample volume extractions, the analyst must increase the quantity of solvent used to maintain the original solvent/sample ratio.

Repeat the extraction twice more and add these extracts to the K-D. Attach a 3-ball Snyder column to the K-D and concentrate the extract on a steam bath to 5-10 mL. Allow the K-D to cool to room temperature and disassemble it, rinsing the Snyder/K-D and K-D/ concentrator joints with 1-2 mL of methylene chloride. Add these rinsings to the extract. Place the concentrator tube into an N-Evap and reduce the volume to 2 mL under a gentle stream of nitrogen. Transfer the extract to a 2 mL autosampler vial fitted with a screw top and a Teflon lined septum. Store the extract in a refrigerator until analyzed.

Along with each sample set, run at least one duplicate sample per set of 10 or fewer samples (10%) and, for each extraction day, at least one method blank (5%). Spiking of surrogates, extraction and analyses of the QC samples will be conducted identically to the regular samples with the exception that organic free water will be used for the method blank.

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

Sample Cleanup: In those cases where samples contain a significant amount of naturally occurring non-petroleum organics, e.g. leaf litter, bark, etc., which may contribute biogenic interferences, the following cleanup technique may be employed to assist in their reduction or elimination.

Transfer the 10 mL sample extract to a 10 to 15 mL centrifuge tube, add 1 mL of concentrated sulfuric acid to the extract and stopper the tube. Mix thoroughly for 1 minute by either shaking the tube or with the use of a vortex-genie adjusted to the highest setting.

Caution: Since sulfuric acid produces a highly exothermic reaction with water and other polar materials, extreme care should be exercised with its use.

Allow the two phases to separate. Centrifugation can be used to facilitate this process. Using a disposable glass pipet, transfer the methylene chloride (top) phase to another centrifuge tube and add approximately 0.4 grams (roughly equivalent to 1 mL of volume) of silica gel to the tube, stopper and mix as before. Allow the silica gel to settle or centrifuge. Repeat the sulfuric acid/silica gel treatment once more. Transfer a portion of the extract to a 2 mL autosampler vial equipped with a Teflon-lined cap and store the extract in a refrigerator until analyzed. A smaller aliquot of the extract may be used for this cleanup procedure as long as the ratio of extract to acid/silica gel is maintained.

It has been noted that some petroleum products, i.e. heavy fuel oils such as #6 fuel oil or Bunker-C, may experience a concentration loss of between 10 and 20 percent when subjected to this cleanup technique. This loss appears to be primarily associated with the removal of petroleum compounds which contain sulfur. To account for this loss when analyzing samples that have been subjected to the cleanup procedure in preparation for heavy fuel oil determination, the analyst must use utilize standards which have undergone the cleanup technique to calibrate the GC.

Note: The use of EPA method 3611 (Alumina column cleanup) may be substituted for the above cleanup technique if it is demonstrated to provide equivalent results.

Analysis Procedure

Prior to the analysis of any samples or method blanks, the analyst must prepare and analyze a mid-range calibration check standard to insure that the instrument is functioning correctly and that the calibration is still valid. The value obtained for this analysis must not vary from the true (known) value by more than plus/minus 15%. If the value falls outside this range then a second mid-range calibration check standard should be analyzed. If the analysis of the second check standard fails to

meet the acceptance criteria, then the instrument must be recalibrated prior to the analysis of any samples. Once the instrument has been shown to be in calibration, the analyses of samples may proceed.

The analyst shall use #2 diesel as the default petroleum product for reporting purposes when no petroleum products were identified in any initial screening or when the type(s) of petroleum products are unknown prior to analysis.

After the last sample has been analyzed, a mid-range calibration check sample must be run to demonstrate that the instrument is still operating within the required parameters. Should this standard fail to meet those parameters, then all samples analyzed after the last successful calibration check standard must be reanalyzed. An increase in the frequency of mid-range calibration check standard analyses beyond the minimum required is recommended.

Qualitative Analysis - Identification

If NWTPH-HCID has not been previously performed on the samples and/or the type of petroleum present is unknown, the analyst should pre-screen the samples to determine the petroleum product. The observed petroleum product shall be determined by pattern matching with the standard(s) analyzed the same day. Chromatograms used for this "fingerprinting" should be normalized to approximately 90% of full scale for the largest component of the particular petroleum product observed.

When reporting the results, the terms such as "diesel range" or "motor oil range", or derivations of them, should only be used when the analyst is unable to identify the petroleum product(s) present. Motor oils, hydraulic fluids and similar petroleum products which consist primarily of an unresolved chromatographic envelope of compounds originating at, or extending beyond tetracosane, may be reported using the collective term "lube oil" unless specific identification is possible. Heavy fuel oils, e.g. #6 fuel oil or Bunker-C, which contain a diesel range component as well as a lube oil range, may be reported using the collective term "heavy fuel oil" unless specific identification is possible. Heavy fuel oils should not, however, be confused with mixtures of #2 diesel and lube oils.

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

Quantitative Analysis - Integration

The retention time range (window) for integration must be adjusted to incorporate the majority of the components of petroleum product(s) identified as present in the samples. If specific product identification can not be made, the analyst must quantitate the samples with the calibration curve for the petroleum product that most closely resembles that of the sample. In all cases, the selected retention time range (windows) used for quantitation must, at a minimum, include any unresolved envelope of compounds as well as all discrete component peaks with an area greater than or equal to 10% of the largest peak. These components must be integrated to the baseline as a group.

For those surrogates which elute within the retention time range used for integration of a petroleum product, the analyst must subtract the area of the surrogate from the total area to yield the appropriate area of the petroleum product. In this case, the analyst may wish to generate separate calibrations for the petroleum standards and the surrogate(s) to facilitate integration and quantitation.

At the discretion of the analyst, the range of components included in the integration may be adjusted in order to minimize the potential contribution of any co-eluting fractions arising from the presence of multiple petroleum products. Any change in the integration range must be reflected in a concomitant change to the calibration standards integration.

Sample chromatograms of various petroleum products are included at the end of this method to assist the analyst in determining the appropriate integration ranges.

Result Calculation

For Soil

$$Soil\ Sample\ Conc,\ mg / kg\ =\ \frac{(A\ x\ R)\ x\ V\ x\ Dilution\ Factor}{E\ x\ W\ x\ S}$$

where

A	=	Area Count from Sample
R	=	Response Factor (ng injected/area count)
V	=	Extract Volume (mL)
W	=	Weight of Sample (g)
E	=	Volume injected, (uL)
S	=	Decimal percent solids of sample

For Water

$$Water\ Sample\ Conc,\ mg / L\ =\ \frac{(A\ x\ R)\ x\ V}{E\ x\ S}$$

where

A	=	Area Count from Sample
R	=	Response Factor (ng injected/area count)
V	=	Extract Volume (mL)
S	=	Volume of Sample (mL)
E	=	Volume Injected (uL)

The recovery of the surrogate should be between 50% and 150% and must be reported with the results. If the recovery of the surrogate is not able to be obtained due to a high levels of petroleum contamination, then this fact needs to be reported.

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