

NWTPH-Gx

Volatile Petroleum Products Method for Soil and Water

Summary

The NWTPH-Gx method is intended to replace the Oregon's TPH-G and Washington's WTPH-G methods and to present a more comprehensive approach to volatile petroleum product analyses. NWTPH-Gx adapts Oregon's TPH, Washington's WTPH and EPA SW846 Methods 5030 and/or 8020 and covers the quantitative and qualitative analyses of volatile petroleum products, e.g. gasolines, naphtha, mineral spirits, stoddard solvent, and other volatile petroleum products in soil and water. Soil samples are extracted with methanol and analyzed by gas chromatograph with a flame ionization detector (GC/FID). The methanol extracts may be injected directly into the GC using or they may be diluted with organic free reagent water and introduced by a purge/trap concentrator. Water samples are introduced directly to the purge/trap concentrator. This method specifies the criteria for the identification and quantitation of volatile petroleum products. When the type of petroleum product is unknown, regular unleaded gasoline will initially be used as the default petroleum standard. The use of GC/PID, GC/MS or GC/AED (Atomic Emission Detector) for the analysis of gasoline may be substituted for GC/FID as long as all other method parameters are met.

The reporting limits for soil are 5 mg/kg by the purge/trap procedure and 20 mg/kg for direct injection. All soil results are reported on a dry weight basis. Since this value assumes 100% solids, the analyst may wish to adjust the amount of soil extracted and/or purge a larger quantity of extract to achieve the reporting limits. For water, the reporting limits are 0.25 mg/L.

The method is applicable for the identification, by pattern matching ("fingerprinting") and quantitation of volatile petroleum products, i.e. those petroleum products for which the majority of the components elute within the gasoline range.

Note: Benzene, Toluene, Ethylbenzene and Xylenes (BTEX) may be determined simultaneously with gasoline if the requirements of EPA Method 8021 or EPA Method 8260 are met (i.e. the use of a PID (Photoionization Detector) for method 8020 or a MS (Mass Spectrometry) for method 8260 and the QA/QC associated with these methods).

This method must be performed by, or under the direct supervision of, analysts experienced in the use of GC and in the interpretation of gas chromatographs of both fresh and weathered volatile petroleum products.

Equipment and Reagents

Gas Chromatograph

Purge/Trap Liquid Concentrator - Tekmar or Equivalent - Autosampler (Optional)

Flame Ionization (FID) or Photo Ionization/Flame Ionization Detectors (PID/FID)

Suggested Capillary Column: Restex RTX-502.2, 60M x 0.53 mm x 3.0 um film thickness or equivalent

Chromatography Data System

Gas tight syringes, various volumes, Hamilton brand or equivalent

Volumetric flasks: 10 mL, ground glass joint with stopper

Methanol: Burdick and Jackson Purge/Trap grade or equivalent

Petroleum Product Standards: Available from commercial sources

Refer to methods 5030 and/or 8020 for the remaining equipment and reagent requirement

Sample Containers/Holding Times

All soil samples for NWTPH-Gx analyses must be collected in soil VOA bottles with Teflon coated septum lined tops. They should be filled to the top to minimize headspace above the soil and stored at 4 degrees C until analyzed. The maximum holding time (the time from the date of collection to the date of analysis) for gasoline and any other volatile petroleum product is 14 days.

All water samples for NWTPH-Gx analyses must be collected in glass VOA vials with Teflon coated septum lined screw tops. They must be filled so that there is no air space (headspace) above the water. Samples should be preserved with 1+1 HCl to a pH <2 and refrigerated at 4 degrees C until analyzed. The maximum holding time (the time from the date of collection to the date of analysis) is 7 days for unpreserved samples and 14 days for preserved samples. The results of any samples which exceed these limits must be qualified as an estimated value.

Standards

Stock Standards. A stock standard is prepared by placing approximately 9 mL of methanol in a 10 mL volumetric flask. Allow the flask to stand, unstoppered, until the methanol wetted surfaces have dried (about ten minutes), then tare the methanol/flask. Add about 5 drops of the petroleum product to the flask while assuring that the liquid falls directly into the methanol without contacting the neck of the flask. Weigh the flask again and dilute to volume with methanol, stopper and mix by inverting the flask several times. The use of commercially prepared standards is acceptable to the above procedure. Commercially prepared gasoline standards must be certified as non-oxygenated gasoline or the gasoline concentration has been adjusted to reflect the contribution of the oxygenate. Calculate the concentration as follows:

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

The standard for gasoline will be regular unleaded gasoline and this standard is to be used as the default petroleum product for reporting purposes.

Note: The use of oxygenated regular unleaded gasoline for this standard is allowed if the weight (mass) of the gasoline used is adjusted for the weight contribution of the oxygenate to the gasoline. This will necessitate the analysis of the gasoline for the specific oxygenate(s) present to determine their concentration. This analysis must 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.

Stock Surrogate Standard

Note: The suggested surrogates are 1,4-difluorobenzene and bromofluorobenzene. The use of additional surrogates is optional. Selected surrogate compounds should be non-polar, purgeable from water and must not coelute with any significant component of gasoline.

Make up a stock standard by accurately weighing the surrogate compound(s) into a 10 mL volumetric flask. Utilize the same procedure as the stock gasoline standard preparation if neat material is used or by adding the appropriate volumes of dilute surrogate if solutions are used. Bring it to volume with

methanol. The use of commercially prepared surrogate solutions is an acceptable alternative to the above procedure.

Working Surrogate Spike. Add the appropriate volume of stock surrogate standard to methanol in a partially filled 10 mL volumetric flask and dilute to volume with methanol. The final concentration of the working surrogate solution is left to the discretion of the analyst, however, this solution should produce between 5 ng and 50 ng of surrogate introduced to the GC.

Secondary Dilution Standard. Using serial dilutions of the stock standard, prepare a 50 ug/mL standard by adding the appropriate volumes, as calculated below, to a 10 mL volumetric flask. The appropriate volume of the stock surrogate standard may also be added to this volumetric flask. Dilute to volume with methanol to yield a final working standard concentration of 50 ug/mL for the standard. Surrogate compound(s) may be added automatically during the sampling process by an autosampler. Gasoline is the default petroleum product for reporting purposes.

$$\text{Stock Std (Gasoline), } \mu\text{L} = \frac{50 \text{ ug / mL} \times 10 \text{ mL}}{\text{Stock Std Conc, ug / mL}} \times \frac{1000 \text{ } \mu\text{L}}{\text{mL}}$$

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

Calibration Standard

The aqueous purge standards are each prepared by adding 5 μL , 10 μL , 20 μL and 50 μL and 100 μL of the secondary dilution standard per 5 mL of organic free water. The five point calibration standard quantities in the purged water are then 250 ng, 500 ng, 1000 ng, 2500 ng and 5000 ng for the volatile petroleum products. At the discretion of the analyst, the concentration of the surrogate can increase with increasing standard concentration or remain at a fixed value for all calibration standards and samples. Extending the calibration range, either up or down, is allowed as long as the standards remain within the linear range of the instrument and a minimum of a five point calibration is produced. 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%.

The use of an autosampler may be substituted for this manual method of standards and sample introduction.

Direction Injection. Prepare calibration standards from the stock gasoline standard and surrogate standards at concentrations of 10 ug/mL, 25 ug/mL, 50 ug/mL, 100 ug/mL and 250 ug/mL for gasoline by adding the appropriate volumes to volumetric flasks and diluting to volume with methanol. Increasing the calibration range with higher standards is acceptable as long as the linear range of the instrument is not exceeded.

Purge/Trap and GC Parameters

Follow the procedure outlined in Method 8021 for the set up of the purge and trap operating parameters and for the GC. Adjust the hydrogen/air flow rates to optimize the FID sensitivity.

Soil Extraction Procedure

Weigh approximately 5 grams of soil into a 40 mL VOA vial and record the weight to 0.001 grams. Add 50 uL of the surrogate working standard and 10 mL of methanol. Quickly cap the vial and shake for 1 minute or use an ultrasonic bath for 2 minutes shaking well after 1 minute. Allow the soil methanol mixture to separate, centrifuging if necessary to clarify the methanol extract. For storage, transfer a portion of the extract into a 2 mL glass autosampler vial, with a Teflon-lined cap, minimizing the headspace and store in a freezer for no longer than one week prior to analysis. Along with the samples, prepare at least one method blank and one sample duplicate per ten samples.

Determine the moisture content of the sample, for use in the final calculations, by the following method. 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 degrees C. Reweigh the sample/crucible after allowing it to cool to room temperature. Calculate the % solids as follows: [(grams of dry sample/grams of wet sample) x 100].

Analysis Procedure

Prior to the analysis of any samples or method blanks, prepare and analyze a mid-range calibration check standard to insure that the instrument is functioning correctly and that the calibration is valid. This standard should be produced daily using the secondary gasoline standard. The value obtained for this analysis must not vary from the true (known) value by more than plus/minus 20%. If the value falls outside this range then a second mid-range calibration standard should be produced and the analysis repeated. If the reanalysis of the fresh standard fails to meet the acceptance criteria, then the instrument must be recalibrated prior to the analysis of any samples. Once the instrument is shown to be in calibration, the analyses of samples may proceed.

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 must either be reanalyzed or the results obtained must be qualified as an estimated value. An increase in the frequency of mid-range calibration check standard analyses beyond the minimum required is recommended.

Significant interferences may be encountered due to the presence of other petroleum products (or non-petroleum products) eluting within the retention time range of the volatile petroleum product being analyzed. If this occurs, the analyst is allowed to adjust the retention time range used for quantitation to exclude the interferences or to subtract the area of the interfering components from the total area prior to the quantity determination. With the former method, the calibration curve must be adjusted in the same manner to reflect the change in retention time range and integration area.

For volatile petroleum products other than gasoline that have a more narrow boiling point range, e.g. mineral spirits, the retention time range used for quantitation should be adjusted to encompass the expected range of the product. Petroleum products which cannot be identified should be quantitated with the gasoline calibration curve. The term "gasoline range" hydrocarbons, or derivations of it, should not be used when reporting the petroleum values unless the analyst is unable to identify the petroleum product present.

Purge/Trap - Soil. A 100 uL aliquot of the methanol extract is transferred via a 100 uL gas tight syringe to 5 mL of organic free water in a 5 mL gas tight syringe and immediately injected into the purging vessel of the purge and trap device. For samples expected to contain concentrations of gasoline range volatiles outside the calibration linear range, or if dilution is required, a smaller aliquot of the methanol extract, or sample, should be used. The analysis then proceeds as in Method 8020. Autosampler techniques may be substituted for this manual method of sample introduction.

Purge/Trap - Water. Sample water (5 mL) is transferred to a 10 mL gas tight syringe and the working surrogate standard spike is added, via a gas tight syringe, into the 5 mL water sample. Immediately inject this water into the purge vessel of the purge/trap device. If necessary, a smaller sample aliquot may be used in order to remain within the linear calibration range of the instrument.

Larger sample volumes may be analyzed, at the discretion of the analyst, if lower quantitation limits are required. Autosampler techniques may be substituted for this manual method of sample introduction.

Direct Injection - For Soil. Allow the extract to come to room temperature, then inject, either manually or by autosampler, 2 uL of the extract into the GC using the splitless injection mode.

Quantitation

The retention time range (window) for gasoline integration must, at a minimum, include toluene through naphthalene. For other volatile petroleum products, the retention time range for integration must be adjusted to incorporate the majority of the components of the 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 of the petroleum product that most closely resembles that of the sample.

For those surrogates which elute within the retention time range used for integration, the analyst must subtract the area of the surrogate(s) from the total area to yield the appropriate area of the petroleum product.

The analyst shall use regular unleaded gasoline 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.

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

Result Calculation

The area of the components is integrated, as a group, to the baseline and compared to concentrations of the standards which are integrated in the same manner.

For Soil

$$\text{Soil Sample Conc, mg / kg} = \frac{(A \times R) \times D}{E \times W \times S}$$

where

A	=	group area of sample
R	=	Response factor from std curve (ng injected/area count)
D	=	Extract Volume, mL
W	=	Weight of sample, grams
E	=	Volume of extract purged or injected, uL

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S = Decimal percent solids of sample

For Water

$$\text{Water Sample Conc, ug / L} = \frac{(A \times R)}{V}$$

where

A = group area of sample
R = Response factor from std curve (ng purged/area count)
V = Volume of sample purged, mL

The recovery of the surrogate should be between 50% and 150% and must be reported with the results. Report any surrogate recoveries that can not be calculated due to a high level of gasoline contamination.

Bob Carrell, Manchester Environmental Laboratory, Dept. of Ecology, State of Washington. This method is based on Oregon's Department of Environmental Quality TPH-G and Washington's Department of Ecology WTPH-G methods.