Volatile Hydrocarbons (VH) in Waters by GC/FID

Parameters

Volatile Hydrocarbons (nC6-nC10) in waters

Analyte Symbols and EMS Codes

Analyte Symbol	Approx MDL	EMS Codes
VH_{w6-10}	300 ug/L	

***Refer to EMS Parameter Dictionary on the ministry website for current EMS codes.

Analytical Method

Purge and Trap, Headspace (Static or Dynamic) - Gas Chromatography with Flame Ionization Detection (GC/FID). PBM

Purge and trap: A portion of the sample is transferred to a purging chamber. The VH are purged from the sample with an inert gas, and are trapped on a solid sorbent trap. The trap is heated and the VH are directed into a gas chromatograph equipped with a FID.

Headspace: A portion of the extract is transferred to a headspace vial containing water. The vial is then sealed and heated and a portion of the headspace above the sample is introduced into a GC/FID.

This method is performance-based. Laboratories may adopt alternative options to improve performance or efficiency provided that all stated performance requirements and prescribed (mandatory) elements are met.

Introduction

This method measures the collective concentration of Volatile Hydrocarbons (VH_W) in water. Volatile Hydrocarbons (VH) are quantitated against either meta-xylene or a mixture of meta- and para-xylenes (m,p-X), and 1,2,4-trimethylbenzene. VH_{W6-10} measures hydrocarbons that elute between n-hexane and n-decane, roughly equivalent to a boiling point range of 69 ^oC to 174 ^oC.

Volatile Hydrocarbons (VH_{W6-10}) is the precursor to the calculation of Volatile Petroleum Hydrocarbons (VPH). Specified Monocyclic Aromatic Hydrocarbon (MAH) results are subtracted from VH concentrations to arrive at VPH, using the procedure outlined in the British Columbia Ministry of Environment, Lab Manual method “Calculation of Volatile Petroleum Hydrocarbons in Solids, Waters or Air (Vapour)”.

The Volatile Hydrocarbons (VH) method is normally used in conjunction with the BC Lab Manual Extractable Petroleum Hydrocarbons (EPH) method. Together, these methods can generate quantitative values for the concentration of most petroleum products. Note that the correlation of these results with the actual concentration of petroleum product in a sample (i.e. accuracy) may be less than would be achieved for single compound analyses.

Petroleum products that are predominantly captured with the VH parameter are those whose primary components are within the boiling point range of nC6 through nC10 (e.g. VH captures the majority of most unweathered gasolines, mineral spirits, and paint thinners). Petroleum products that are predominantly captured with the EPH parameters are those whose primary components are within the boiling point range of nC10 through nC32 (e.g. EPH captures the majority of most diesel fuels, lubricating oils, greases, hydraulic oils, waxes). Many petroleum products contain components within both the VH and EPH parameter ranges (e.g. kerosenes, jet fuel, and weathered gasolines). Petroleum products that contain a substantial proportion of hydrocarbons with boiling points greater than nC32 will not be accurately quantitated by either of the VH or EPH methods.

In addition to quantitative numerical results, this method generates FID chromatograms that can sometimes be used to characterize the type of petroleum hydrocarbon mixture present in the sample.

This method contains numerous prescribed (required) elements, but it is otherwise a Performance Based Method (PBM). Prescriptive elements are included where necessary to maintain consistency of VH results among laboratories. British Columbia Ministry of the Environment (BCMOE) encourages method innovations and supports the performance based methods approach, but recognizes that the application of performance based methods to method-defined aggregate parameters like Volatile Hydrocarbons is somewhat limited.

Every laboratory that uses this method, or a modified version of this method, to report VH_{W6-10} or VPH data to BCMOE must perform an in-house validation of the method as described in the method validation requirements section.

The GC/FID analysis portion of this method is not intended to quantitate individual target compounds (i.e. MAHs). GC/MS is strongly recommended for quantitation of target compounds, although FID may be more appropriate in cases where sample concentrations exceed the GC/MS calibration range and where interferences are not evident.

A dual column GC system with both FID and MS detectors is strongly recommended for this method, so that VH can be determined simultaneously along with targeted MAH parameters like BTEX, styrene, and naphthalene. Analyzing VH and MAHs from the same sample aliquot reduces the impact of sub-sampling variability on the final VPH result.

Method Summary

Purge and trap: A portion of the sample is transferred to a purging chamber. The VH are purged from the sample with an inert gas, and are trapped on a solid sorbent trap. The trap is heated and the VH are directed into a gas chromatograph equipped with a flame ionization detector (FID).

Headspace: A portion of the extract is transferred to a headspace vial containing water. The vial is then sealed and heated to a pre-determined temperature for a given period of time. After equilibration, a portion of the headspace above the sample is introduced into a GC/FID. The sample may be focused onto a solid sorbent trap prior to being desorbed onto the GC column.

This is a Performance Based Method (PBM) with many prescriptive elements included where necessary to maintain consistency of results among laboratories.

Matrix

Fresh Water, Waste Water, Marine Water.

Interferences and Precautions

Contaminants present in solvents, reagents and sample processing hardware may cause interferences or yield artifacts. All of these must be monitored and demonstrated to be free of interferences under the conditions of the analysis by the routine analysis of method blanks.

This method does not differentiate naturally occurring hydrocarbons from petroleum based hydrocarbons, nor does it differentiate hydrocarbons from complex organics.

This method requires the analysis of a representative sub-sample of the total contents of each sample container, including (where possible) any hydrocarbons which may be present as solids or adsorbed to solids within the sample container, but excluding any hydrocarbons which may be adsorbed to the surface of the sample container.

Contamination by carryover from the GC or the Purge and Trap system can occur whenever high-level and low-level samples are sequentially analyzed. If possible, when an unusually concentrated sample is analyzed, it should be followed by an Instrument Blank to check for system cleanliness. Alternatively, low-level samples that follow such high level samples must be re-analyzed if carryover is suspected.

Any component of the purge gas flow path within the Purge and Trap system can be subject to contamination, and may sometimes require bake-out and/or replacement.

Excessive methanol decreases purge efficiency, can prevent resolution of hexane from the solvent peak, and may cause difficulties with the adsorptive trap and with chromatography. Do not add more than a total of 100 uL of methanol to any sample or calibration standard, and ensure that all samples and calibration standards are closely matrix matched with respect to methanol concentration.

The purging efficiency of aqueous solutions is influenced by pH and ionic strength. Therefore, all samples and calibration standards must be matrix matched with respect to preservatives.

The toxicity and carcinogenicity of chemicals used in this method have not been precisely defined. Treat all chemicals used in this method as a potential health hazard. To ensure your personal safety and the safety of co-workers, read and understand the Material Safety Data Sheets (MSDS) for all chemicals used.

Sample Handling and Preservation

Collect samples in 40 mL glass screw-cap vials with Teflon-lined silicone septa. Collect samples with zero headspace.

Preserve all samples using one of the following procedures:

a) Add 200 mg of solid sodium bisulfate to each 40mL vial (to a pH of ~ 2), or

b) Add a few drops of 1:1 HCl or H_2SO4 to each 40mL vial (to a pH of ~ 2)

At least two replicate samples should be taken for each sample location. This allows the laboratory to analyze Field Replicates as desired, and/or to re-analyze any sample if confirmation is required.

Stability

Holding Time: Maximum holding time prior to analysis is 14 days after sampling if preserved. Where holding times are exceeded, data must be qualified.

Storage Conditions: Store samples at ≤ 10˚C during shipment to lab, and at ≤ 6˚C at the laboratory in an area free from organic solvent vapors.

Apparatus

Glassware and Support Equipment
Glass sparge vessels (5 mL fritted spargers recommended)
Micro-syringes
5 mL glass syringe with wide-bore entry port (not a syringe with a needle)
Headspace vials and caps

Gas Chromatograph (GC)
A temperature programmable capillary gas chromatograph is required. A heated split/splitless or on-column inlet is recommended. The data station must be capable of storing and reintegrating chromatographic data and must allow integration of peak areas using a forced baseline projection.

Detector
A Flame Ionization Detector (FID) is required for the quantitation of VH_{W6-10}. The FID is the most universal detector for petroleum products, generating nearly equivalent response by weight or concentration for most hydrocarbons.

Sample Introduction Mechanism

Purge and Trap conditions:	SW846 Method 5030C
Static Headspace conditions:	SW846 Method 5021A

Chromatographic Column
The reference column for this method is a 30 meter, 0.53 mm internal diameter capillary column with a 1.5um coating of 100% dimethyl siloxane (e.g. DB-1, HP-1, RTX-1 or equivalent). The stationary phase type may not be modified.

Procedure

Headspace: An appropriate amount of sample is added to a clean headspace vial. Internal standards are added, either manually or automatically by the headspace system. Sample vials are sealed with a cap and Teflon-lined septum, and are introduced to the headspace heating system, where they are allowed to establish a partition equilibrium. Mechanical vibration may be used to accelerate the process. The vial may be pressurized with an inert gas. A representative fraction of headspace is transferred to the analytical trap or directly to the GC column via a heated transfer line or syringe.

Purge and trap: An appropriate amount of sample is added to a clean purge and trap vial. Internal standards are added, either manually or automatically by the purge and trap system. Sample vials are sealed with a cap and Teflon-lined septum, and are loaded onto the autosampler. VHs are purged from the samples with an inert gas, and are trapped on a solid sorbent trap. The trap is rapidly heated and the contents are transferred to the GC column via a heated transfer line.

Samples must be matrix-matched with calibration standards and QC samples in terms of the solvent/preservative used.

GC-FID Analysis

Analyze samples by GC-FID. Split/Splitless inlets are recommended but on-column or other inlets may be used if QC and relative response requirements are met.

FID was chosen for this method because FID is the most universal detector for hydrocarbons and generates nearly equivalent response by weight or concentration for most hydrocarbons and other organic compounds (more so than any other detector).

Example GC-FID Conditions

The following GC-FID conditions are provided as an example only. Any conditions that meet specified QC and relative response requirements are acceptable. GC phase type must be 100% dimethylpolysiloxane.

Column:	100% dimethylpolysiloxane (e.g. DB-1), 30 m, 0.53 mm id, 1.5 µm phase
Carrier Gas:	helium
Head pressure:	9.0 psi @ 40˚C (with column dimensions as specified)
Column flow:	15 mL/minute @ 40˚C (88 cm/sec linear velocity)
Constant flow:	recommended
Injector temp:	200˚C

Injection mode:	split
GC liner type:	2 mm id splitless liner no glass wool
Inlet purge on time:	1.0 minute (splitless)
FID temperature:	250˚C
Oven program:	Initial Temp 40˚C (hold 4.0 minutes) 5˚C /min to 140˚C (no hold) 25˚C /min to 220˚C (hold 2.0 minutes)

Reagents and Standards

Reagents

Acetone (2-propanone)
Methanol - Purge and Trap grade
Organic-free reagent water - Refer to US EPA (3) Method 524.2, section 7.2.2.
Preservatives – one of the following is required:

- Hydrochloric acid (HCl), diluted 1:1 with reagent water
- Sulfuric acid (H2SO4), diluted 1:1 with reagent water
- 200mg sodium bisulfate per 40mL sample
- 10% Copper Sulfate (CuSO4.5H2O) by weight in reagent water

Aliphatic hydrocarbons are poorly soluble in methanol, especially when cold. Ensure that all calibration standards and reference solutions are warmed to room temperatures and mixed well prior to use to ensure complete dissolution of all components. Store all standards refrigerated at ≤ 6 ˚C. Storage in a freezer is preferable.

Calibration Standards

Prepare a minimum of 3 levels of Calibration Standards in methanol, each containing n hexane (nC6), n-octane (nC8), n-decane (nC10), benzene, toluene, ethylbenzene, meta xylene, para-xylene (optional), ortho-xylene, and 1,2,4-trimethylbenzene (124-TMB). If both meta- and para-xylenes are included in calibration standards, it is recommended that they be present at half the concentration of the other constituents.

Calibration Verification Standard (CVS)

Prepare a CVS containing meta-xylene (or meta- and para-xylenes) and 1,2,4-trimethylbenzene in methanol at a concentration near the middle of the calibration curve. It must be prepared from a source independent from the Calibration Standard (both standards may originate from the same neat compound source, but they must not be prepared from the same intermediate solutions).

Gasoline Stock Standard

Prepare a stock solution of gasoline in methanol (e.g. 10,000 µg/mL). Prepare the solution by weight (e.g. weigh 0.250 g gasoline into a 25 mL volumetric flask). Record the source of the gasoline used. A gasoline source that does not contain ethanol is recommended. Note that the nominal concentration of gasoline (weight gasoline / volume) is not equal to the concentration of $VH_{w6\text{-}10}$ (the nominal gasoline concentration is higher).

Detection Limit Check Standard

Dilute the Gasoline Stock Solution to prepare a Detection Limit (DL) Check Standard in methanol. Prepare the standard at a concentration that is approximately equal to the extract concentration that corresponds to the Reporting Detection Limit for $VH_{w6\text{-}10}$. This standard is required for Initial Calibration QC.

Quality Control

All required calibration and QC components of this method are summarized in the table below. Each of these components is described in detail in this section.

Summary of VH_W QC and Calibration Requirements		
QC Component	**Minimum Frequency**	**Data Quality Objectives***
Instrument Performance QC		
Instrument Performance Check	Every 12 hours, and at end of analysis batch if >6 hrs from previous check.	Relative response ratios must be 0.7-1.3 for all components.
Calibration QC and Verification		
Instrument Blank	1 per initial calibration	None; required for background correction.
Calibration Verification Standard (CVS)	1 per initial calibration	Within 15% of expected concentration.
Detection Limit Check Standard	1 per initial calibration	50 – 150% of VH target.
Continuing Calibration Verification (CCV)	Every 12 hours, and at end of analysis batch if >6 hrs from previous check.	Within 20% of initial calibration
Method QC		
Method Blank	1 per 20 samples (1 per batch minimum)	< Reported Detection Limit.
Laboratory Control Sample (Gasoline Method Spike)	1 per 20 samples (1 per batch minimum)	70-130% recovery
Laboratory Duplicates	1 per 20 samples (1 per batch minimum)	30% RPD
Surrogate Compounds	All samples	70-130% recovery **
Field QC		
Travel Blank	Recommended	Not specified
Field Duplicates	Recommended	Not specified

* DQOs apply at levels above 10x MDL. Laboratories should report qualified data when DQOs are not met.

** Surrogate DQOs do not apply when samples contain high levels of hydrocarbons that interfere with the measurement of the surrogate. Non-measureable surrogate recoveries due to interference does not indicate a data quality issue.

Instrument Performance QC

Instrument Performance Check

REQUIRED. Perform this check whenever a Calibration Standard or Verification Standard is analyzed. See the Continuing Calibration Verification (CCV) section for required frequency.

Instrument Performance Check are used to do the following:

A. Measure and control relative response ratios of specified VH components,
B. Determine retention time windows for VH integration ranges, and
C. Confirm resolution of hexane (nC6) from the solvent peak.

The essential purpose of the Instrument Performance Check is to ensure that the

GC/FID response factors of VH components throughout its boiling point range are roughly equal. If excessive relative bias exists among VH components due to differences in their polarity, mass, boiling point, or chemical composition, then calculated results will be biased, and interlaboratory inconsistency will result.

For each component of the Calibration Standard, determine the relative response ratio (by peak area) against the appropriate reference compound. Compare the peak areas of hexane (nC6), octane (nC8), benzene, toluene, and ethylbenzene against meta-xylene (or meta- and para- xylenes). Compare the peak areas of decane (nC10) and o-xylene against 1,2,4-trimethylbenzene. Acceptance criteria for relative response ratios are 0.7 – 1.3. If any relative response ratio fails these acceptance criteria, associated sample data is suspect and corrective action is required. Loss of response of any of the compounds in the mixture may indicate that GC maintenance is necessary.

Calibration QC

Instrument Blank (IB)
REQUIRED. Minimum 1 per initial calibration. Inject a matrix matched blank to the GC system to establish the chromatographic baseline.

Calibration Verification Standard (CVS)
REQUIRED. Minimum 1 per initial calibration.

Analyze a CVS (see the Calibration Verification Standard section) containing meta-xylene (or meta- and para-xylenes) and 1,2,4-trimethylbenzene, which has been prepared from a different source than the Calibration Standard. The CVS is used to confirm the integrity of the calibration standard.

If the calculated concentration of meta-xylene (or meta- and para-xylenes) or 1,2,4-trimethylbenzene in the CVS varies by more than 15% from the expected target, then the calibration is invalid. Discrepancies must be corrected before any sample results for the analysis batch may be reported. Correction may require any or all of:

a) Re-analysis of CVS and/or Calibration Standard.
b) Re-preparation and re-analysis of CVS and/or Calibration Standard.
c) GC maintenance (if discrepancy is due to calibration non-linearity).

Detection Limit Check
REQUIRED. Minimum 1 per initial calibration. The sensitivity of the GC system at the Reporting Detection Limit must be verified regularly using a low level solution of gasoline.

Analyze a Detection Limit Check Standard that contains VH_{W6-10} at a concentration that is approximately equivalent to the VH_{W6-10} Reported Detection Limit for the method (see the Detection Limit Check Standard section). Acceptable performance for the Detection Limit Check Standard is between 50 - 150 % of the VH_{W6-10} target.

Method QC

Method Blank (MB)
REQUIRED. Minimum 1 per preparation batch of no more than 20 samples. Prepare a Method Blank using reagent water.

If a Method Blank result is above a Reported Detection Limit for a sample within a preparation batch, the data report for that sample must be qualified (it may be acceptable to increase the Reported Detection Limit of affected sample results to a level above that of the Method Blank result).

Laboratory Control Sample (LCS)
REQUIRED. Minimum 1 per 20 samples. Prepare a Gasoline LCS by fortifying reagent water with an accurate volume of a Gasoline Method Spike Solution, which should be prepared at a concentration at least 10x the laboratory's reported detection limit.

Determine the target for VH_{w6-10} by directly analyzing several replicates of the Gasoline Method Spike Solution diluted to a concentration that equals the amount of gasoline spiked (in µg) divided by the volume of reagent water used for the spike.

Acceptable performance for the Laboratory Control Limit sample is between 70 - 130 % of the VH_{W6-10} target.

Laboratory Duplicates
REQUIRED. Minimum 1 per 20 samples. Laboratory duplicates should be conducted by sub-sampling a second aliquot from a single field sample. Laboratory Duplicates must be subjected to all sample preparation steps experienced by samples. Acceptable performance for the laboratory duplicate sample is between 30 % Relative Percent Difference (RPD).

Surrogate Compounds
REQUIRED. The use of one or more surrogate compounds for VH is required. Surrogate(s) must be added to each sample prior to the extraction or instrumentation process. Surrogates that elute outside the VH retention time range are recommended so that they do not need to be subtracted from integrated VH peak areas.

2,4-Dichlorotoluene is recommended as a VH surrogate compound, but any suitable surrogate compound may be used (2,4-Dichlorotoluene lies slightly beyond the VH range, which simplifies the integration of VH peak areas). Because VH surrogates are measured by GC-FID, which is less selective and less sensitive than GCMS, it is recommended for VH surrogate concentrations to be 10-100 times higher than GCMS surrogates.

VH surrogates may be combined with surrogates required for VOC/BTEX analyses (if required) when running in dual simultaneous GCMS/FID mode.

Positive interferences from high concentration volatile hydrocarbons in a sample may sometimes preclude the accurate measurement of FID surrogates. This does not indicate a data quality issue. Do not report a recovery where a Surrogate Compound cannot be accurately measured due to a co-eluting interference (report "n/a").

Field QC

Travel Blank
RECOMMENDED. Travel Blanks/Trip Blanks are useful to verify contamination that could be introduced during travel or storage.

Field Duplicates
RECOMMENDED.

Instrument QC

Instrument blank
REQUIRED. Minimum 1 per initial calibration. Inject a matrix matched blank to the GC system to establish the chromatographic baseline.

Calibration Verification Standard (CVS)
REQUIRED. Minimum 1 per initial calibration. Analyze a CVS (see the Calibration Verification Standard section) containing meta-xylene and 1,2,4-trimethylbenzene, which has been prepared from a different source than the Calibration Standard. The CVS is used to confirm the integrity of the calibration standard. Acceptance criteria are 85-115%.

Detection Limit Check
REQUIRED. Minimum 1 per initial calibration. Analyze a Detection Limit Check Standard that contains VH_{W6-10} at a concentration that is approximately equivalent to the VH_{W6-10} Reporting Detection Limit for the method (see the Detection Limit Check Standard section). Acceptable performance for the Detection Limit Check Standard is between 50 - 150 % of the VH_{W6-10} target

Calibration & Analysis Procedure

Initial Calibration
A minimum 3 point linear external standard calibration is required for this method.

For each analysis batch, verify that the GC system is performing adequately by conducting all checks specified in the Instrument Performance QC section (see the Instrument Performance QC section).

Calculate the Calibration Factors (CFs) for meta-xylene and 1,2,4-trimethylbenzene in the Calibration Standard using the equation below:

CF_{m-X} (mL/µg) = m-X area / [m-X] (µg/mL)

$CF_{124-TMB}$ (mL/µg) = 124-TMB area / [124-TMB] (µg/mL)

Continuing Calibration Verification (CCV)
After initial calibration, the Calibration Factors (CF_{m-X} and $CF_{124-TMB}$) must be verified, at minimum, after every 12 hours of continuous operation, by re-analysis of a Calibration Standard. The calibration must also be verified at the end of each analysis batch if more than 6 hours has passed since the previous verification.

An initial calibration is valid as long as both Calibration Factors remain within 20% of their initial values.

See the Instrument Performance Check section for Instrument Performance QC requirements that must be satisfied with each Calibration Standard and Verification Standard.

Integration of Total Areas for VH_{W6-10}
VH_{w6-10} is defined to include all GC/FID peaks eluting between hexane (nC6) and decane (nC10). VH_{w6-10} is quantitated by summing the results for two sub-ranges within the nC6-nC10 range. The first VH sub-range falls between the retention times of hexane and ortho-xylene. The second VH sub-range falls between the retention times of ortho-xylene and decane. Each sub-range is integrated and quantitated separately, and VH_{w6-10} is then calculated by summing the two results.

Note: Calculating VH using two sub-ranges reduces the impact of relative response biases which may exist between higher and lower volatility VH components. The two-range calculation mechanism was intended to simplify the development of purge and trap methods that may be equivalent to alternate methods such as the headspace injection method.

Determine the total integrated peak area of each VH sub-range, where:

a) The $VH_{w(6-oX)}$ range begins at the apex of the nC6 peak and ends at the apex of the o-xylene peak.
b) The $VH_{w(oX-10)}$ range begins at the apex of the o-xylene peak and ends at the apex of the nC10 peak.

Retention times of the marker compounds must be updated or verified with each analysis batch.

Peak integration must include all peaks, whether resolved or not, that are above the

chromatographic baseline, as established by instrument blanks within the analysis batch.

Automated software integrations of VH areas must be visually verified, and must be manually corrected where integration error appears to exceed approximately 2%.

$VH_{w6\text{-}10}$ is the sum of the calculated concentrations for $VH_{w(6\text{-}oX)}$ and $VH_{S(oX\text{-}10)}$. $VH_{w(6\text{-}oX)}$ is quantitated against the meta-xylene (or meta- and para-xylene) calibration standard. $VH_{w(oX\text{-}10)}$ is quantitated against the 1,2,4-trimethylbenzene calibration standard.

It is highly recommended that the Surrogate Compounds used for VH analysis elute slightly outside the VH range of nC6 – nC10. If any Surrogate Compounds are added to samples within the VH range, the contribution to VH of those Surrogates must be subtracted from calculated VH results.

Use the following equations to calculate $VH_{w6\text{-}10}$:

$VH_{W6\text{-}10}$ (ug/mL) = $VH_{W(6\text{-}oX)}$ (ug/mL) + $VH_{W(oX\text{-}10)}$ (ug/mL) - Actual Surr. Conc* (ug/mL)

* Only Surrogates (if any) that elute within the $VH_{W6\text{-}10}$ range are subtracted.

$$VH_{W(6\text{-}oX)}\ (ug/mL) = \frac{A_{(6\text{-}oX)} \times Vol}{CF_{m\text{-}Xylene}}$$

$$VH_{W(oX\text{-}10)}\ (ug/mL) = \frac{A_{(oX\text{-}10)} \times Vol}{CF_{1,2,4\text{-}Trimethylbenzene}}$$

where:

$A_{(6\text{-}oX)}$	= Total area between nC6 and ortho-xylene for the sample chromatogram.
$A_{(oX\text{-}10)}$	= Total area between ortho-xylene and nC10 for the sample chromatogram.
$CF_{m\text{-}Xylene}$	= Calibration Factor for meta-xylene standard (ug-1).
$CF_{1,2,4\text{-}Trimethylbenzene}$	= Calibration Factor for 1,2,4-trimethylbenzene standard (ug-1).
Vol	= Volume of sample purged (mL).

Dilution Requirement for High Level Sample Extracts

All valid sample analyses must lie within the validated linear range of the GC/FID system, based on initial validation. Any samples that exceed the validated linear range must be diluted and re-analyzed (for purge and trap or headspace, dilution normally entails re-analysis using a smaller aliquot of the sample).

Method Validation Requirements

Initial Method Validation requirements as outlined below must be completed before this method may be used to generate $VH_{W6\text{-}10}$ results for unknown samples.

Initial Verification of Relative Response Requirements

Before proceeding with further validation steps, verify that the GC-FID method meets the relative response requirements of the method by performing the Instrument Performance Check (see the Instrument Performance QC section).

Calculation of Actual VH_W Concentrations of a Gasoline Reference Solution

This procedure describes how to calculate the Actual $VH_{W6\text{-}10}$ Concentrations for aqueous solutions of petroleum products where only the total weight/volume concentration of the petroleum product in the water is explicitly known. Actual $VH_{W6\text{-}10}$ concentrations of a petroleum product solution can only be measured experimentally, whereas the concentration of the petroleum product in the water is simply determined by dividing the weight of product by the volume of water in which it is prepared.

Actual VH_{W6-10} Concentrations are required within this method for the following purposes:

a) Determination of GC/FID linear range for VH_{W6-10} (i.e. calibration range).
b) Determination of VH_{W6-10} Instrument Detection Limits (IDLs).
c) Preparation of DL Check Standards and Method Spike Solutions.
d) Calculation of VH_W targets for DL Check Standards and Method Spike Solutions.

Use the following procedure to calculate the *Actual VH_{W6-10} Concentration* of a reference gasoline:

a) Prepare the petroleum product in aqueous solution at a concentration at least 20x greater than the estimated Instrument Detection Limits for VH_{W6-10}. A petroleum product concentration of at least 5 ug/mL in water is recommended for this purpose

b) Perform replicate analyses of the aqueous petroleum product solution prepared in (a) using the instrumental conditions specified within this method. A minimum of 7 replicates is recommended. Do not dilute the solution prior to analysis. Determine the average measured concentration of VH_{W6-10} using the calculations specified in section 15. In the example below, the measured VH_{W6-10} concentration is denoted as [VH_{W6-10},measured], where the square brackets denote concentration. Percent Relative Standard Deviations (%RSDs) of these values may also be determined, and may be useful to set statistical warning and control limits for some applications.

c) Calculate the percentage that the VH_{W6-10} range represents of the total petroleum product concentration. Example (for a given source of gasoline):

$$\%VH_{W6-10} \text{ in gasoline} = 100\% \times \frac{[VH_{W6-10,measured}]}{[Gasoline_{grav}]}$$

where:

[ ]	= symbol for concentration
[VH_{W6-10}, measured]	= measured [VH_{W6-10}] of a solution of gasoline in water.
[$Gasoline_{grav}$]	= actual [Gasoline] in weight of gasoline / volume water for the same solution
Units	= same for both concentrations (e.g. ug/mL).

Note: The percentage of VH_{W6-10} in gasoline is considerably less than 100% (typically about 50%) because not all components of gasoline fall within the nC6 - nC10 boiling point range.

d) To calculate the *Actual VH_{W6-10} Concentrations* of other concentrations of the same product, use the VH_{W6-10} percentage relative to the total petroleum product concentration as follows (the gasoline example is continued):

$$\textit{Actual } VH_{W6-10} \textit{ conc. in gasoline} = \frac{(\%VH_{W6-10} \text{ in gasoline})}{100\%} \times [Gasoline_{grav}]$$

Where [$Gasoline_{grav}$] = the conc. of gasoline (in wt. gasoline / volume water) of any solution

Establish Instrument Calibration Working Range and Estimated IDLs
Establish the linear working range of the GC/FID system for VH_{W6-10} using a series of dilutions of the 50,000 ug/mL Gasoline Stock Solution into water. Analyze gasoline solutions at concentrations ranging from below the estimated Instrument Detection Limit to above the estimated maximum calibration concentration in approximately 2-fold increments. The following aqueous concentrations are recommended as an approximate guide: 0.02, 0.05, 0.1, 0.5, 1, 2, 5, 10, 25, 50, and 100 ug/mL of the gasoline solution. Calculate VH_{W6-10} results for each solution using the procedure described in the calculations section. These are referred to below as *Calculated VH_{W6-10} Results*.

Make a plot of *Calculated VH_{W6-10} Results* (y-axis) versus *Actual VH_{W6-10} Concentrations* (x-axis), and determine the linear working range of VH_{W6-10}.

At the Limit or Reporting, VH_{W6-10} should be measureable at 50-150% of the expected concentration.

The upper range of the validated linear range must be used to determine when over-range samples must be diluted.

Note: Validation of upper linear range is particularly important for purge and trap methods.

Establishing Method Detection Limits
Determine the Method Detection Limits (MDLs) at the 95% confidence level for VH_{W6-10}, using the procedure outlined in the British Columbia Environmental Laboratory Manual or a comparable reference.

Select a concentration for method spikes of gasoline into reagent water of between one and three times the estimated IDL for VH_{W6-10}. Prepare and analyze at least 7 method spikes at this concentration. Use a Gasoline Spike Solution to prepare these method spikes (see Method QC section).

Calculate the Method Detection Limit (MDL) at the 99% confidence level for VHS6-10.

Average recoveries of the MDL Method Spikes for VH_{W6-10} must be between 60 - 140%, where recovery is defined as calculated VH_{W6-10} result / target VH_{W6-10} concentration, as determined in the Calculation of Actual VH_W Concentration of a Petroleum Reference Solution section. If this condition is not met, repeat the MDL determination at a higher spike level.

Determination of DL Check Standard Concentration and VH Targets
Use the procedure that follows to select a suitable aqueous concentration of gasoline for the DL Check Standard. This procedure involves the conversion of gasoline product concentration units to (and from) VH_{W6-10} concentration units (in aqueous solution).

a) Calculate the percentage of the total gasoline concentration that VH_{W6-10} represents, using the procedure described above. Typically, VH_{W6-10} represents about 50% of the total gasoline concentration. This percentage is less than 100% because not all components of gasoline fall within the nC6 - nC10 boiling point range.

b) Determine the concentration of gasoline in water that corresponds to the VH_{W6-10} Reporting Detection Limit. Use the calculated percentage from (a) to calculate this gasoline concentration:

[Gasoline in water] equiv. to VH_{W6-10} DL = 100 x $\frac{\text{(Reporting DL for } VH_{W6-10})}{(\%VH_{W6-10} \text{ in Gasoline})}$

Where [Gasoline] and VH_{W6-10} Reporting DLs must be in the same units (e.g. ug/mL of water).

Select a concentration for the Detection Limit Check Standard that is approximately equal to the concentration determined above.

Example: For a Reporting Detection Limit of 100 ug/L VH_{W6-10} with a sample size of 5 mL, add 10 uL of a 100 ug/mL solution of gasoline to 5 mL of reagent water to achieve a 200 ug/L aqueous concentration of gasoline in the check standard. If the proportion of VH_{W6-10} in the gasoline is 50%, then the aqueous concentration of VH_{W6-10} in the Detection Limit Check Standard will be 100 ug/mL

c) Calculate the target for VH_{W6-10} in the Detection Limit Check Standard by multiplying the concentration selected in (b) by the VH_{W6-10} percentage from (a).

Target for VH_{W6-10} = (DL Std. gasoline concentration in water) x ($\%VH_{W6-10}$ in gasoline)

Accuracy and Precision Requirement:
A minimum of 8 Laboratory Control Samples prepared from unweathered gasoline must be used to assess the accuracy and precision of the method. Determine Method Spike targets using *Actual VH_{W6-10} Concentrations* of the spike solution by following the procedure outlined in section the Calculation of Actual VH_W Concentration of a Petroleum Reference Solution section. The minimum accuracy requirement for Initial Validation is an average recovery of 80-120%. The minimum precision requirement for Initial Validation is a Relative Standard Deviation of ≤ 20%

Method Performance Data

Single laboratory and interlaboratory performance data for this method were published in previous versions of the BC Lab Manual. Refer to the 2013 version or earlier versions of the BC Lab Manual to access this information.

Use of Alternative Methods

This method contains many prescribed and required elements that may not be modified. These requirements are necessary due to the nature of method-defined aggregate parameters like Volatile Hydrocarbons, where many components are calculated against single calibration reference standards. This method has been specifically designed to minimize the relative bias among responses of common VH components, and among VH_{W6-10} results generated by different laboratories.

Modification or omission is not permitted to anything described within the method text as “required” or preceded by the word “must”. Most of the prescribed requirements of the method are summarized in the Prescribed Elements section

Prescribed Elements

Laboratories that report data for regulatory purposes may not alter any method conditions listed in this section without prior written permission from BC MOE:

a) Every laboratory that uses this method, whether modified or not, must validate the method (as used) following the protocols described in the Method Validation section.
b) “REQUIRED” QC elements from the Quality Control section must be completed as specified, and must pass all specified acceptance criteria, or sample data must be qualified.
c) Sample Handling and Preservation guidelines may not be modified.

d) Gas Chromatography with Flame Ionization Detection is required for VH_{W6-10}.

e) GC column must be a capillary column, with 100% dimethylpolysiloxane stationery phase (e.g. DB-1, HP-1, RTX-1 or equivalent).

f) Meta-xylene (or meta and para xylenes) and 1,2,4-trimethylbenzene must be used as the calibration standards for VH_{W6-10}. Minimum 3 point linear calibration is required.

g) GC calibration standard must be matrix matched, unless equivalence (within 2%) can be demonstrated for component responses and retention times of Instrument Performance Checks in alternative solvents.

h) Calibration stability must be monitored as described in the Continuing Calibration Verification (CCV) section.

i) VH_{W6-10} method detection limits and reporting limits must be based on unweathered gasoline (see the Establishing Method Detection Limits section).

Performance Based Method Changes

This is a Performance Based Method. Unless prohibited in the Prescribed Elements section or where instructions are prefaced by the words "required" or "must", modifications to this method are permitted, provided that the laboratory possesses adequate documentation to demonstrate an equivalent or superior level of performance. Laboratories that modify this method must achieve all specified Quality Control requirements, and must maintain on file the Standard Operating Procedures that describe any revised or alternate methods used. This information must be available in the event of audit by BC MOE.

The Instrument Performance Checks of this method are designed to identify potential sources of instrument and method biases. Any modified method that cannot achieve the performance requirements of these QC checks is not equivalent to the reference method.

The required QC elements contained within this method are deemed sufficient to identify potential biases introduced by permitted modifications within these areas of the method.

References

i) US EPA Method 5030C, Purge and Trap for Aqueous Samples, Revision 3, May 2003.

ii) US EPA Method 5035A, Closed System Purge and Trap Extraction for Volatile Organics in Soil and Waste Samples, Revision 1, July 2002.

iii) US EPA Method 5021A, Volatile Organic Compounds in Soils and Other Solid Matrices using Equilibrium Headspace Analysis, Revision 1, June 2003.

iv) CPPI (Canadian Petroleum Products Institute), Inter-Laboratory Study #3 to Evaluate the Analytical Variability of Volatile Organics, Phenol, and Sulfide Procedures, CPPI Report No. 92-1, March 1992.

Revision History

Mar 9, 2017	Revised to new format. Removed Purge & Trap as prescriptive element. Allowed for Headspace analysis. Requirement for Method Performance Spike was replaced with new requirement to run Laboratory CVS's (gasoline) with each batch. Meta-Xylene calibration standard was clarified such that meta/para-Xylene mixtures may also be used. Maximum batch size changed from 50 to 20 samples to coincide with industry standard practice. Calibration changed to minimum 3 point linear with narrower 20% CCV requirement. Preservative options updated to include sodium bisulfate, copper sulfate preservative option deleted.
April 2007	Hold time updated.

Dec 31, 2000	Method incorporated into main Laboratory Manual; reformatting to match style of Lab Manual; EMS codes and units added; phrase ‘Analyte Code’ changed to ‘Analyte Symbol’. Mandatory tests made bold. Former methods superseded.
July 1999	Finalization of present method based on results of a vetting round robin.
1998 - 1999	Revision of method by ASL under contract to MELP and with advice from the BCLQAAC Technical Committee.
March 1997	Initial publication of Version 1.0 for Volatile Petroleum Hydrocarbons in Water.