Volatile Hydrocarbons in Soil by GC/FID

Parameter

Volatile Hydrocarbons$_{(nC6\text{-}nC10)}$ in soil or solids

Analytical Method

Methanol Extraction - Gas Chromatography with Flame Ionization Detection (GC/FID).

Introduction

This method measures the aggregate concentration of Volatile Hydrocarbons in soils or other solids (VH_S). Volatile Hydrocarbons (VH) are quantitated in two sub-ranges, using either meta-xylene or a mixture of meta- and para-xylenes (m,p-X) for the first sub-range, and using 1,2,4-trimethybenzene (124-TMB) for the second sub-range. $VH_{S6\text{-}10}$ measures hydrocarbons that elute between n-hexane and n-decane, roughly equivalent to a boiling point range of 69 ˚C to 174 ˚C.

Volatile Hydrocarbons ($VH_{S6\text{-}10}$) 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 Lab Manual method “Calculation of Volatile Petroleum Hydrocarbons in Solids, Waters, or Air (Vapour) - VPH”.

Petroleum products that are predominantly captured by VH are those whose primary components are within the boiling point range of nC6 through nC10, for example gasolines, mineral spirits, and petroleum naphtha. The volatile fraction of some heavier petroleum products like kerosenes, jet fuels, and diesels can also be partially captured by VH.

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

The GC/FID analysis portion of this method is not intended to quantitate individual target compounds (i.e. VOCs). However, the methanol extract produced by this method can and should be used for the analysis of targeted VOCs by selective detector (GC/MS is strongly recommended).

Method Summary

Solid samples are either field-extracted/preserved in methanol (typically ~ 5 grams of wet soil is extracted into exactly 10.0 mL methanol), or core samples of wet soil (typically 5 grams) are collected in the field using a hermetic sampler prior to methanol extraction at the laboratory.

Extracts are directly analyzed by capillary column gas chromatography with flame ionization detection (purge and trap or headspace sample introduction may also be used).

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.

MDL and EMS Codes

Analyte	Approximate MDL	EMS Code
$VH_{S6\text{-}10}$	20 mg/kg (Direct Injection) 5 mg/kg (Purge and Trap, Headspace)	VHC- F084

Matrix

Soil, Sediment, Solids

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.

Where the proportion of water in a methanol extract exceeds 20-25%, the solubility of non-polar organics in the extract is substantially diminished (especially when refrigerated). A ratio of 2:1 methanol to wet solids is targeted to minimize the water content of methanol extracts. With the use of field methanol extraction and hermetic samplers, it is difficult to precisely control this ratio, but the laboratory must add methanol if necessary to ensure this ratio is at least 1.5 : 1. A higher ratio of approximately 2:1 or more is recommended for high moisture samples (e.g. > 50% moisture content).

Detection limits increase for samples with high moisture contents.

Pure petroleum samples are not applicable to the extraction and preservation components of this method, but may be analyzed by the VH analytical procedures. Most middle-distillate or heavier petroleum products (diesels, oils, etc.) are immiscible with methanol, but can be dissolved in acetone, which can then be diluted with methanol prior to analysis by standard VH analytical protocols, if blanks are analyzed to control any interferences from acetone.

Soil samples that are highly contaminated with heavy oils (e.g. oil soaked soils) may be poorly extracted by methanol. If such samples are encountered and identified, they should alternatively be extracted with acetone or with a mixture of acetone and methanol. Dilution of acetone or acetone/methanol extracts prior to analysis may be necessary. Analyze an appropriate blank to control interferences from acetone.

Sample Handling and Preservation

Samples must be collected and processed by one of the following two options:

i) **Field Methanol Preservation Option:** A representative sub-sample of soil (typically ~ 5 grams wet weight) is collected in the field and is extracted and preserved into an exactly known volume of high purity methanol (typically 10.0 mL). Two preserved sub-sample vials per sample are recommended as a precaution against leaks, breakage, or error.

ii) **Hermetic Sampler Option:** A representative sub-sample of soil (typically ~ 5 grams wet weight) is collected in the field using a hermetically sealed soil sampling device.

Soil samples or methanol may become contaminated if exposed to or stored in the presence of gasoline or solvent vapours or automotive exhaust.

Immediately after sampling, hermetic samples and methanol preserved samples should be refrigerated or stored in coolers with sufficient quantities of ice or ice packs to ensure that sample temperatures will not exceed 10 °C during transit to the laboratory, and must be refrigerated at ≤ 6 °C after receipt by the laboratory (preferably frozen at ≤ -7 °C).

Verification of Field Methanol Preservatives

Laboratories must ensure that Quality Control procedures are in place to ensure that Field Methanol preservatives they provide are fit for purpose. On a routine or batch basis, tare weights and methanol volumes of pre-dispensed and pre-weighed methanol vials must be verified (recommended specifications are +/- 2% of methanol volume and +/- 0.1 grams for pre-weights). Small errors in methanol volume or tare weights can cause larger errors in final test results.

Stability

Holding Time – Hermetic Samplers: Hermetic samplers must be methanol extracted within **48 hours** of sampling. Hold time prior to methanol extraction can be extended to 7 days from sampling if sample is frozen (≤ -7 °C) within 48 hours of sampling, but frozen samples must be extruded into methanol while still predominantly or partially frozen.

Holding Time – Methanol Extract: 40 days from sampling date.

Storage Conditions: Methanol extracts must be stored in the laboratory at ≤ 6 °C (preferably ≤ -7 °C).

Sample Preparation

This procedure is required for the analysis of both targeted VOCs and the aggregate parameter, VHs6-10. The same extract should normally be used to analyze all of these parameters.

Take an aliquot of the soil sample from the soil jar to perform an accurate moisture determination on the sample, so final results can be provided in dry weight units.

Hermetically Sealed Samplers
Keep hermetic samplers at ≤ 6 °C (preferably frozen) until immediately prior to extraction. Frozen samples should be extruded to methanol while still predominantly or partially frozen (warm for ~2-3 minutes at room temperature to facilitate extrusion).

Transfer the entire contents of the hermetic sampler to a tared vessel and accurately weigh the contents to at least the nearest 0.01 grams.

Add an exact volume of high purity methanol (typically 10 mL per 5 gram sample), equal to approximately 2 times the wet weight of the soil sample (but no less than 1.5 times the wet weight of the soil sample). Pre-charged methanol vials of known weight may be used.

Field Methanol Preserved Samples
Weigh field methanol preserved sample vials at the laboratory to at least the nearest 0.01 grams. Determine the accurate weight of wet soil or solids in each sample from the weight (*vial + methanol + soil sample)* minus the pre-weight *(vial + methanol)*.

Prior to weighing, carefully clean the outside of the sample vials to remove any adhered soil or residues. The weights of any labels that may have been affixed to sample vials must be considered when calculating sample weights.

Confirm that the ratio of methanol to wet weight of soil is at least 1.5 : 1. If not, accurately add additional methanol, targeting a ratio of approximately 2:1 (or higher). Record the volume of additional methanol added to at least the nearest 0.1 mL.

Methanol Extraction and Agitation (All Samples)
Prepare appropriate and required Method QC samples as described in the Method QC section.

At least one surrogate compound is recommended for VH analysis. VH surrogates may be combined with surrogates required for VOC/BTEX analyses (if required). Surrogates should be added to every sample (in methanol solution) prior to agitation. Surrogates will highlight possible problems with analyses, or with limitations of the extraction process (e.g. adsorption of VOCs by charcoal or organic carbon in soil samples).

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.

Field methanol preserved samples must be physically agitated using a mechanical shaker (e.g. wrist shaker or platform shaker) for at least 15 minutes.

Hermetic samples that are methanol extracted in the laboratory must be physically agitated using a mechanical shaker (e.g. wrist shaker or platform shaker) for at least 60 minutes.

After the agitation process, let suspended solids settle by gravity or centrifuge if necessary. Transfer all or a portion of the extract to a vial for refrigerated storage. Store remaining extract at ≤ 6 ˚C for at least 40 days in case re-analysis is required.

GC-FID Analysis

Analyze methanol extracts by GC-FID. The simplest technique for this analysis is direct injection GC-FID, for which conditions are described below.

Direct injection GC-FID is appropriate where reported detection limits of approximately 20 mg/kg or higher are required. Purge and trap GC-FID analysis is suitable where reported detection limits of lower than approximately 20 mg/kg are required. Headspace GC-FID may also be used if all performance specifications of the method are met. Refer to the BC Lab Manual method for VH in Water for detailed purge and trap conditions.

Samples must be matrix-matched with calibration standards and QC samples in terms of the amount of methanol present.

Caution: Refrigerated extracts must be warmed to room temperature and mixed gently before use or before sub-sampling (non-polar aliphatic sample components are insoluble in methanol at cold temperatures).

Recommended Direct Injection GC-FID Conditions

Column:	100% dimethylpolysiloxane (e.g. DB-1), 30 m, 0.53 mm id, 1.5 um phase
Carrier Gas:	helium
Head pressure:	5.0 psi @ 36˚C (with column dimensions as specified)
Column flow:	7.5 mL/min (50 cm/sec linear velocity)
Constant flow:	recommended
Injector temp:	200˚C
Injection solvent:	methanol
Injection volume:	1 uL (higher volumes tend to cause GC backflash)
Injection mode:	splitless or on-column
GC liner type:	4mm id splitless liner with silanized glass wool
Inlet purge on time:	0.3 minutes (splitless)
FID temperature:	250˚C
Oven program:	Initial Temp 36˚C (hold 3.0 minutes) 5˚C /min to 150˚C (no hold) 15˚C/min to 240˚C (hold 6.0 minutes)
FID gas flows:	as recommended by manufacturer

Standards

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). For the direct injection method, concentrations of 20, 50, and 250 µg/mL are recommended. 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.

Control Standard
Prepare a Control Standard 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 Solution
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 $VH_{S6\text{-}10}$ (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 $VH_{S6\text{-}10}$. This standard is required for Initial Calibration QC.

Quality Control

Table I-14 summarizes all required calibration and QC components of this method. Each of these components is described in detail in this section.

Table I-14: Summary of VH_S QC and Calibration Requirements

QC Component	Minimum Frequency	Data Quality Objectives
Instrument Performance QC		
Instrument Performance Check	Daily at beginning of each analysis batch, repeated at least every 24 hours.	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.
Control Standard	1 per initial calibration	Within 15% of expected concentration.
Detection Limit Check Standard	1 per initial calibration	50 – 150% of VH target.
Ongoing Verification of Calibration	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)	40% RPD
Field QC		
Travel or Field Blank (Field Methanol Technique only)	Strongly Recommended (1 per sampling event)	< Reported Detection Limit
Field Duplicates	Recommended	None

* Minimum DQOs apply at levels above 10x MDL. Report qualified data if DQOs are not met.

Instrument Performance QC

Initial Performance Check

REQUIRED. Perform this check whenever a Calibration Standard or Verification Standard is analyzed. See the Ongoing Verification of Calibration (Verification Standards) 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. 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.

Initial Calibration QC

Instrument Blank

REQUIRED. Minimum 1 per initial calibration. Inject a methanol solvent blank to the GC system to establish the chromatographic baseline.

Control Standard

REQUIRED. Minimum 1 per initial calibration.

Analyze a Control Standard (see the Control 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 Control Standard is used to confirm the integrity of the calibration standard.

If the calculated concentration of meta-xylene or 1,2,4-trimethylbenzene in the Control Standard 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 Control Standard and/or Calibration Standard.
b) Re-preparation and re-analysis of Control Standard 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_{S6-10} at a concentration that is approximately equivalent to the VH_{S6-10} 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_{S6-10} target.

Method QC

Method QC samples are carried through all stages of sample preparation and measurement. They are intended to measure average method performance over time, and to control method performance under a statistical process control model.

Method Blank

REQUIRED. Minimum 1 per preparation batch of no more than 20 samples. Prepare a Method Blank using a clean soil/sediment matrix (or using reagents only).

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

REQUIRED. Minimum 1 per 20 samples. Prepare a Gasoline LCS by fortifying a clean soil matrix (containing approximately 20% 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 $VH_{S6\text{-}10}$ 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 final extract volume for the spike (i.e. the volume of methanol plus volume of water).

Laboratory Duplicates

REQUIRED. Minimum 1 per 20 samples. Laboratory duplicates should be conducted by sub-sampling the same methanol extract from a single field sample (e.g. from a single field methanol extraction vial or from a single hermetic sampler).

Surrogate Compounds

RECOMMENDED. The use of one or more Surrogate Compounds for VH is recommended. Surrogate(s) should be added to each sample prior to the extraction or mechanical agitation 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 suitable surrogate compound).

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 or Field Blank (Field Methanol Technique only)

STRONGLY RECOMMENDED. Travel Blanks and/or Field Blanks are important to verify purity of supplied methanol vials including storage, transit, and field effects. Travel Blanks can identify problems with tare weights of vials (including leakage issues), methanol contamination issues, methanol volume errors, and contamination that could be introduced during travel or storage. Field Blanks (which must be opened and handled similarly to a sample in the field) can potentially also identify contamination due to the field sampling environment (e.g. due to high concentrations of hydrocarbon or gasoline vapours). Field Blanks are recommended for sampling environments where hydrocarbon or solvent vapours may be present at time of sampling.

Field Duplicates

RECOMMENDED.

Instrument QC

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

Control Standard
REQUIRED. Minimum 1 per initial calibration. Analyze a Control Standard (see the Control Standard section) containing meta-xylene and 1,2,4-trimethylbenzene, which has been prepared from a different source than the Calibration Standard. The Control Standard 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_{S6-10} at a concentration that is approximately equivalent to the VH_{S6-10} 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_{S6-10} target.

Calibration & Analysis Procedure

Initial Calibration
A minimum 3 point linear external standard calibration is required for this method. 20, 50, and 250 µg/mL concentrations of meta-xylene (or m,p-xylenes) and 1,2,4-trimethylbenene are recommended for the direct injection method (see the Calibration Standard section).

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)

Ongoing Verification of Calibration (Verification Standards)
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_{S6-10}
VH_{S6-10} is defined to include all GC/FID peaks eluting between hexane (nC6) and decane (nC10). VH_{S6-10} 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_{S6-10} 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 the direct injection method described here.

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

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

$VH_{S6\text{-}10}$ is the sum of the calculated concentrations for $VH_{S(6\text{-}oX)}$ and $VH_{S(oX\text{-}10)}$. $VH_{S(6\text{-}oX)}$ is quantitated against the meta-xylene (or meta- and para-xylene) calibration standard. $VH_{S(oX\text{-}10)}$ 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 $VH_{S6\text{-}10}$:

$$VH_{S6\text{-}10}\ (\mu g/g) = VH_{S(6\text{-}oX)}\ (\mu g/g) + VH_{S(oX\text{-}10)}\ (\mu g/g)$$
$$VH_{S(6\text{-}oX)}\ (\mu g/g) = (A_{(6\text{-}oX)} \times TEV \times Dil) / (CF_{m\text{-}X} \times DryWt)$$
$$VH_{S(oX\text{-}10)}\ (\mu g/g) = (A_{(oX\text{-}10)} \times TEV \times Dil) / (CF_{124\text{-}TMB} \times DryWt)$$

where:

$A_{(6\text{-}oX)}$ = Total area between nC6 and ortho-xylene
$A_{(oX\text{-}10)}$ = Total area between ortho-xylene and nC10
$CF_{m\text{-}X}$ = Calibration Factor for m-X or m,p-X standard (mL/µg)
$CF_{124\text{-}TMB}$ = Calibration Factor for 124-TMB standard (mL/µg)
Dil = Dilution factor of sample extract (unitless)
DryWt = Dry weight of sample extracted (g)
TEV = Total Extract Volume, including sample moisture, $H2O_{samp}$ (mL)
$H2O_{samp}$ = Sample Wet Weight Extracted x %Moisture (mL)

TEV is approximated by summing the volumes of water due to moisture + methanol, as follows:

TEV = (water due to sample moisture, $H2O_{samp}$, mL) + (methanol volume, mL)

Report test results for $VH_{S6\text{-}10}$ in solids samples in units of mg/kg (ppm, dry weight basis).

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 methanol extract).

Method Validation Requirements

Initial Method Validation requirements as outlined below must be completed before this method may be used to generate $VH_{S6\text{-}10}$ results for unknown samples.

Initial Verification of Relative Response Requirements

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

Calculation of Actual [VH_S] of a Gasoline Reference Solution

This procedure describes how to calculate the *Actual $VH_{S6\text{-}10}$ Concentrations* for solutions of petroleum products where only the total weight/volume concentration of the petroleum product is explicitly known. *Actual $VH_{S6\text{-}10}$ concentrations* of a petroleum product solution can only be measured experimentally, whereas the nominal concentration of the petroleum product in the solution is simply determined by dividing the weight of product by the volume of solvent in which it is prepared.

Actual $VH_{S6\text{-}10}$ Concentrations are required within this method for the following purposes:

a) Determination of GC/FID linear range for $VH_{S6\text{-}10}$ (i.e. calibration range).
b) Determination of $VH_{S6\text{-}10}$ Instrument Detection Limits (IDLs).
c) Preparation of DL Check Standards and Method Spike Solutions.
d) Calculation of VH_S targets for DL Check Standards and Method Spike Solutions.

Use the following procedure to calculate the *Actual $VH_{S6\text{-}10}$ Concentration* of a reference gasoline:

a) Prepare a reference gasoline solution at a concentration at least 20x greater than the estimated Instrument Detection Limits for $VH_{S6\text{-}10}$ (see the Establishing Instrument Calibration Working Range and Estimated IDLs section). A petroleum product concentration of at least 5,000 µg/mL is recommended for this purpose. This concentration is referred to in the example below as *[Gasoline].*

b) Perform a minimum of 3 replicate analyses of the petroleum product solution prepared in (a) using the selected GC-FID method conditions. In the example below, the measured $VH_{S6\text{-}10}$ concentration is denoted as *[$VH_{S6\text{-}10,measured}$]*.

c) Calculate the percentage that the $VH_{S6\text{-}10}$ range represents of the total petroleum product concentration. Example (for a given source of gasoline):

   $\%VH_{S6\text{-}10}$ in gasoline = 100% x *[$VH_{S6\text{-}10,measured}$]* / *[Gasoline]*

   where:

   $[VH_{S6\text{-}10,\ measured}]$ = measured $VH_{S6\text{-}10}$ concentration (µg $VH_{S6\text{-}10}$ / mL methanol)
   [Gasoline] = nominal gasoline concentration (µg gasoline /mL methanol)

   Note: The percentage of $VH_{S6\text{-}10}$ in gasoline is 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 $VH_{S6\text{-}10}$ Concentrations* of other concentrations of the same gasoline source, multiply the nominal gasoline concentration of the solution by the $\%VH_{S6\text{-}10}$ determined above.

Establish Instrument Calibration Working Range and Estimated IDLs

Establish the linear working range of the GC/FID system for $VH_{S6\text{-}10}$ using a series of dilutions of the Gasoline Stock Solution prepared in methanol. 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. For the direct injection method, the following solution concentrations are

recommended as an approximate guide: 25, 50, 100, 200, 500, 1,000, 2,500, 5,000, 10,000, 20,000, and 50,000 µg/mL of gasoline. Calculate VH_{S6-10} results for each solution using the procedure described in the Calculations section.

At the Limit or Reporting, VH_{S6-10} 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 99% confidence level for VHS6-10, using the procedure outlined in the British Columbia Environmental Laboratory Manual [e] or a comparable reference.

Consider the normal total extract volume produced by this method (including sample moisture), and select a concentration for method spikes of gasoline into a clean soil matrix (containing at least 20% moisture) that should result in extracts with concentrations of between one and three times the estimated IDL for VHS6-10 (as determined in the Establishing Instrument Calibration Working Range and Estimated IDLs section). Prepare, extract, and analyze at least 7 method spikes at this concentration. Use a Gasoline Method Spike Solution to prepare these method spikes.

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

Average recoveries of the MDL Method Spikes for VHS6-10 must be between 60 -140%, where recovery is defined as calculated VHS6-10 result / target VHS6-10 concentration, as determined in the Calculation of Actual VHS 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_{S6-10} Target
Use the procedure that follows to select a suitable concentration of gasoline in methanol for the DL Check Standard. This procedure involves two separate conversions of units:

a) Gasoline product concentration units must be converted to (and from) VH_{S6-10} concentration units.
b) Sample concentration units (e.g. µg/g of solids) must be converted to sample extract concentration units (e.g. µg/mL of methanol).

Results from the Calculation of Actual VH_S Concentration of a Petroleum Reference Solution section and the Establishing Instrument Calibration Working Range and Estimated IDLs section may initially be used for step (a), but this determination should be repeated if the source of the gasoline changes:

a) Calculate the percentage of the total gasoline concentration that VH_{S6-10} represents, using the procedure described in the Calculation of Actual VH_S Concentration of a Petroleum Reference Solution section. Typically, VH_{S6-10} represents about 50% of the total gasoline concentration, because not all components of gasoline fall within the nC6 - nC10 boiling point range.

b) Determine the concentration of gasoline in methanol that corresponds to the VH_{S6-10} Reporting Detection Limit. Use the calculated percentage from (a) to calculate this gasoline concentration. The normal sample volume extracted, an “average” sample moisture content, and the normal methanol extract volume are all required to convert method units to the *equivalent* solution concentration units. Use an average sample moisture content of 20% for calculation purposes:

[Gasoline] equiv. to $VH_{S6\text{-}10}$ DL = 100 x (Reporting DL for $VH_{S6\text{-}10}$) / (%$VH_{S6\text{-}10}$ in Gasoline) x Avg. Sample Dry Weight / Avg. Total Extract Volume

where:

Units for [Gasoline] = ppm (µg/mL of methanol)
Units for Reporting DL for $VH_{S6\text{-}10}$ = ppm (e.g. µg/g dry weight of sample)
Units for Sample Weight = grams (dry weight)

For 20% moisture, 5 wet gram sample weights, and 10 mL Methanol volumes:

Average Dry Sample Weight = 4.0 grams
Average Total Extract Volume = 11.0 mL

Select a concentration for the Gasoline DL Check Standard that is approximately equal to the concentration determined above. The DL Check Standard can then be routinely used to verify that the Reporting Detection Limit for $VH_{S6\text{-}10}$ remains valid.

c) Calculate the target for $VH_{S6\text{-}10}$ in the Detection Limit Check Standard by multiplying the concentration selected in (b) by the $VH_{S6\text{-}10}$ percentage from (a).

Target for $VH_{S6\text{-}10}$ = (DL Std. gasoline concentration in methanol) x (%$VH_{S6\text{-}10}$ in gasoline).

Accuracy and Precision
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 $VH_{S6\text{-}10}$ Concentrations* of the spike solution by following the procedure outlined in section the Calculation of Actual VH_S Concentration of a Petroleum Reference Solution section. The minimum accuracy requirement for Initial Validation is an average recovery of 85-115%. The minimum precision requirement for Initial Validation is a Relative Standard Deviation of ≤ 15%.

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 $VH_{S6\text{-}10}$ 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) Methanol extraction is required (except for samples that form 2 liquid phases with methanol, in which case acetone must be used – see the Interferences and Precautions section).

e) The ratio of methanol to wet weight of solids being extracted must always be at least 1.5:1.

f) Gas Chromatography with Flame Ionization Detection is required for VH_{S6-10}.

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

h) Meta-xylene (or meta and para xylenes) and 1,2,4-trimethylbenzene must be used as the calibration standards for VH_{S6-10}. Minimum 3 point linear calibration is required.

i) GC calibration standard must be prepared in the same solvent as sample extracts, unless equivalence (within 2%) can be demonstrated for component responses and retention times of Instrument Performance Checks in alternative solvents.

j) Calibration stability must be monitored as described in the Ongoing Verification of Calibration (Verification Standards) section.

k) Soil moisture content must be considered within data calculations for the total methanol extract volume for each sample.

l) VH_{S6-10} 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.

Modifications Where Equivalence Testing is Not Required

Except where expressly disallowed in the Prescribed Elements section or elsewhere, changes to the following components of this method are permitted if all specified quality control requirements of the method are achieved:

a) Reagents and Standards
b) Gas Chromatograph Conditions – including the use of Headspace or Purge and Trap analysis.

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) ASTM D6418-09, Standard Practice for Using the Disposable En Core Sampler for Sampling and Storing Soil for Volatile Organic Analysis.

Revision History

Aug 15, 2014	Revised to reflect new requirements for field methanol extraction or hermetic samplers. Minimum ratio of methanol to wet soil changed from 2:1 to 1.5:1. Relative response requirements changed to 0.7-1.3 to coincide with CCME method. Requirement to run Method Performance Spike was replaced with new requirement to run Laboratory Control Standards (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. Laboratory Duplicate DQO changed from 30 to 40% RPD as per QA section guidelines and VOC soil method. Effective date for this revision is Nov 1, 2014.
April 2007	Revision of hold times and preservation requirements.
Dec 31, 2000	SEAM codes replaced by EMS codes. Out of print reference deleted. Method incorporated into main Laboratory Manual; reformatting to match style of Lab Manual; EMS codes and units added; Mandatory tests made bold.
July 1999	Finalization of method (revised by ALS under contract to BC MOE) based on results of round robin vetted by BCLQAAC.
March 1997	Initial publication of Version 1.0 for Volatile Petroleum Hydrocarbons in Solids.