Volatile Organic Compounds in Soil – PBM

Parameter

Volatile Organic Compounds (VOCs) in solids.

Analytical Method

Purge and Trap, Headspace (Static or Dynamic), or Direct Injection - GC/MS or GC/PID (PBM).

Introduction

This method is applicable to the quantitative determination of volatile organic compounds in soil and other solids, when appropriately sampled and extracted with methanol. Analysis for VHs6-10 is often conducted concurrently.

Method Summary

To minimize loss of VOCs during sampling and transport to the laboratory, samples must be either preserved in the field with methanol or collected using hermetically sealed sampling devices. Another aliquot of sample is required for moisture content determination. A field/travel blank (an additional vial pre-charged with methanol) is highly recommended.

Purge and trap: A portion of the extract is transferred to a vial containing water. The VOCs are purged from the sample with an inert gas, and are trapped on a solid sorbent trap. The trap is heated and the VOCs are directed into a gas chromatograph equipped with a mass spectrometric detector (GC/MS). GC/PID is acceptable for a subset of analytes, e.g. BTEX and styrene.

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. After equilibration, a portion of the headspace above the sample is introduced into a GC/MS. The sample may be focused onto a solid sorbent trap prior to being desorbed onto the GC column. GC/PID is acceptable for a subset of analytes, e.g. BTEX and styrene.

Direct Injection: A portion of the extract is transferred to an autosampler vial, and is injected into a GC inlet (typically a split/splitless or on-column inlet), for direct analysis by GC/MS.

The analytical portion of this method is performance-based. Laboratories may adopt alternative options to improve performance or efficiency if all stated performance requirements and prescribed (mandatory) elements are met.

MDL(s) and EMS Analyte Codes

The analytes listed below represent the volatile substances regulated in the 2017 CSR. The MDLs listed below are achievable by GC/MS in a typical laboratory environment, but may vary by laboratory, and with the sample introduction technique used. Ensure that the detection limits reported by the laboratory are sufficient to meet any applicable regulatory standards.

Analyte	Approx. MDL (mg/kg)	CAS Number	EMS Analyte Code
acetone	0.2*	67-64-1	A005
acrolein	0.1*	107-02-8	-
acrylonitrile	0.1*	107-13-1	-
allyl alcohol	0.1*	107-18-6	-
allyl chloride	0.1*	107-05-1	C056
benzene	0.01	71-43-2	B020
benzyl chloride	0.1*	100-44-7	-
bromobenzene	0.01	108-86-1	B005
bromodichloromethane	0.01	75-27-4	B012
bromoform	0.01	75-25-2	B013
bromomethane	0.02*	74-83-9	-
butadiene, 1,3-	0.05*	106-99-0	-
butanol, n-	0.1*	71-36-3	-
butylbenzene, n-	0.01	104-51-8	B034
butylbenzene, sec-	0.01	135-98-8	B035
butylbenzene, tert-	0.01	98-06-6	B036

carbon disulfide	0.05*	75-15-0	-
carbon tetrachloride	0.01	56-23-5	C034
chlorobenzene	0.01	108-90-7	C010
chlorobutane, 1-	0.01	109-69-3	-
chloroethanol, 2-	0.1*	107-07-3	-
chloroform	0.01	67-66-3	C032
chloroprene	0.05	126-99-8	-
chlorotoluene, 2-	0.01	95-49-8	2CLT
chlorotoluene, 4-	0.01	106-43-4	C047
crotonaldehyde, trans-	0.1*	4170-30-3	-
dibromo-3-chloropropane, 1,2-	0.02*	96-12-8	B038
dibromochloromethane	0.01	124-48-1	C033
dibromoethane, 1,2-	0.01	106-93-4	B029
dichlorobenzene, 1,2-	0.01	95-50-1	-
dichlorobenzene, 1,3-	0.01	541-73-1	-
dichlorobenzene, 1,4-	0.01	106-46-7	-
dichlorodifluoromethane	0.02*	75-71-8	-
dichloroethane, 1,1-	0.01	75-34-3	C021
dichloroethane, 1,2-	0.01	107-06-2	C022
dichloroethylene, 1,1-	0.01	75-35-4	C024
dichloroethylene, cis-1,2-	0.01	156-59-2	C063
dichloroethylene, trans-1,2-	0.01	156-60-5	C023
dichloromethane	0.05	75-09-2	M041
dichloropropane, 1,2-	0.01	78-87-5	C025
dichloropropane, 1,3-	0.01	142-28-9	-
dichloropropene, cis-1,3-	0.01	10061-01-5	C027
dichloropropene, trans-1,3-	0.01	10061-02-6	C028
diethyl ether	0.1*	60-29-7	-
dioxane, 1,4-	0.2*	123-91-1	-
ethyl acetate	0.1*	141-78-6	-
ethylbenzene	0.01	100-41-4	B021
hexachlorobutadiene	0.05*	87-68-3	HCBD
hexachloroethane	0.05*	67-72-1	-
hexanone, 2-	0.1*	597-78-6	H024
isobutanol	0.1*	78-83-1	-
isopropanol	0.1*	67-63-0	-
isopropylbenzene	0.01	98-82-8	I008
methacrylonitrile	0.1*	126-98-7	M028
methyl acetate	0.1*	79-20-9	-
methyl ethyl ketone [MEK]	0.1*	78-93-3	B033
methyl methacrylate	0.1*	80-62-6	M054
methyl-tertiary butyl ether [MTBE]	0.02	1634-04-4	MTBE
propylbenzene, 1-	0.01	103-65-1	P030
styrene	0.02*	100-42-5	S010
tetrachloroethane, 1,1,1,2-	0.01	630-20-6	-
tetrachloroethane, 1,1,2,2-	0.01	79-34-5	C080
tetrachloroethylene	0.01	127-18-4	T030
toluene	0.02	108-88-3	T001
trichloro-1,2,2-trifluoroethane, 1,1,2-	0.02*	76-13-1	-
trichloroethane, 1,1,1-	0.01	71-55-6	T016
trichloroethane, 1,1,2-	0.01	79-00-5	T017
trichloroethylene	0.01	79-01-6	T029
trichlorofluoromethane	0.02*	75-69-4	T070
trichloropropane, 1,1,2-	0.01	598-77-6	-
trichloropropane, 1,2,3-	0.01	96-18-4	T067
trichloropropene, 1,2,3-	0.01	96-19-5	-
trimethylbenzene, 1,3,5-	0.02	108-67-8	T069
vinyl acetate	0.05*	108-05-4	-
vinyl chloride	0.05*	75-01-4	C004

xylene, meta+para	0.02	108-38-3 106-42-3	X003
xylene, ortho	0.01	95-47-6	X002

*Analytes with an asterisk in the MDL exhibit known difficulties with reproducibility, response, recovery, stability, and/or chromatography that may reduce the overall quality or confidence in the result. Refer to EPA reference methods 5030/5021/8260 for additional information.

Where appropriate, the method may be used for other compounds not listed here, subject to validation and achievement of data quality objectives (DQOs).

EMS Method Code(s)

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

Matrix

Soil, Sediment, and other solids

Interferences and Precautions

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

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.

Detection limits may be elevated for samples with high moisture content (~ > 50%).

Calibration standards are prepared using methanolic standard solutions. Ensure that samples and standards are matrix-matched as closely as possible with respect to methanol content, unless it can be demonstrated that performance is not compromised. Excessive amounts of methanol can compromise the performance of sorbent traps and/or the mass spectrometer.

Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. If possible, when an unusually high-level 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 above a Reporting Detection Limit is suspected.

Sample Handling and Preservation

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

i) Field Methanol Preservation: A representative sub-sample of soil (typically ~ 5 g wet weight) is collected (typically with a disposable coring device) and extruded into a known volume of high purity methanol (typically 10 mL) contained in a pre-weighed vial.

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

Methanol extracts and hermetic samplers must be immediately chilled at time of collection to ≤ 10˚C for shipment to the laboratory.

Stability

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

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 the sample must be extruded into methanol while still predominantly or partially frozen (warm for ~2-3 minutes at room temperature to facilitate extrusion).

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

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 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 g 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. 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 two surrogate compounds are required for VOC/BTEX analysis. VH surrogates may be combined with surrogates required for VOC/BTEX analyses (if required). Surrogates must 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).

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.

Analysis Procedure

A summary of the analytical procedure follows. Detailed instrumental procedures are described in the following US Environmental Protection Agency methods:

Purge and Trap conditions:	SW846 Method 5030C
Static Headspace conditions:	SW846 Method 5021A
GC/MS conditions:	SW846 Method 8260C
GC/PID conditions:	SW846 Method 8120B

Headspace: An appropriate amount of water is added to a clean headspace vial, followed by an aliquot of sample methanol extract. Addition of salts to equalize aliphatic/aromatic headspace partitioning equilibria is recommended. 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 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 water is added to a clean purge and trap vial, followed by an aliquot of methanol extract. 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. VOCs 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.

Direct Injection: An appropriate volume of internal standards is added to a known volume of sample methanol extract. Samples are dispensed to autosampler vials, and are injected into a GC/MS inlet (typically a split/splitless or on-column inlet), either manually or by autosampler.

Note: For samples containing concentrations of VOCs where one or more analytes exceed the linear range of the analytical system, use a smaller aliquot of methanol extract. It is recommended that additional methanol be added so that the total amount of methanol in the vial remains consistent.

Initial GC/MS calibrations must be five points or more (no more than one point may be excluded). At least two Internal Standards must be used. Continuing calibrations may be employed while Calibration Verification Standards meet acceptance criteria for all reported compounds.

Raw results (i.e. µg/L or µg purged) are converted into final results (mg/kg) by accounting for the sample dry weight, total extract volume (amount of methanol + sample moisture), and analysis aliquot and/or dilution factor. VOCs in solids are normally reported on a dry-weight basis.

Performance Requirements

Any analytical method options selected for this analysis must meet or exceed the method validation performance requirements specified below:

Accuracy and Precision requirements apply to measures of long term method performance (averages and standard deviations). Achievement of these requirements is to be demonstrated during initial and ongoing method re-validation studies. They do not constitute acceptance criteria or Data Quality Objectives for individual Quality Control samples.

For Initial Validations, averages of at least 8 Lab Control Samples must be assessed (preferably taken from multiple analytical batches). Ongoing Re-validations (performance reviews) should assess QC data encompassing longer timeframes (e.g. 1 year). A minimum frequency of 2 years is recommended for Ongoing Re-validations.

Accuracy Requirement: Laboratories must demonstrate method accuracy (measured as average recovery) through repeat analysis of Lab Control Samples at concentrations above ten times the MDL. Average accuracy must be between 80-120%, except 75-125% for the asterisked VOCs (refer to MDL column in analyte table), and any other VOC analytes not listed in this method.

Precision Requirement: Laboratories must demonstrate method precision through repeat analysis of Lab Control Samples at concentrations above ten times the MDL. Precision must be ≤ 20% relative standard deviation (%RSD) for all routinely reported parameters.

Where the laboratory's method does not meet these accuracy or precision requirements for specific parameters, the method may still be used, but reports must indicate that results are semi-quantitative or qualitative, and the established performance should be provided.

Sensitivity Requirement: Where possible, the method should generate Method Detection Limits that are less than 1/5 of applicable numerical standards. The method is not fit-for-purpose if an MDL exceeds a guideline, standard, or regulatory criteria against which it will be used for evaluation of compliance.

Quality Control

Summary of QC Requirements		
QC Component	**Minimum Frequency**	**Minimum Data Quality Objectives**
Internal Standard Area Checks	All samples and QC	Area counts must be 50-200% of the initial calibration CVS
Surrogates	All samples and QC	60-140% recovery
Calibration Verification Standard (CVS)	1 per initial calibration	80-120% recovery
Field Blank or Trip Blank (Field Methanol Technique only)	Strongly Recommended 1 per sampling event	Less than reported DL
Method Blank (MB)	1 per batch (max 20 samples)	Less than reported DL
Lab Control Sample (LCS)	1 per batch (max 20 samples)	60-140% recovery (50-150% for asterisked and non-listed analytes – see analyte table)
Matrix Spike (MS) or Reference Material (RM)	1 per batch (max 20 samples)	60-140% recovery (50-150% for asterisked and non-listed analytes – see analyte table)
Lab Duplicates	1 per batch (max 20 samples)	≤ 50% RPD [or within 2x reported DL for low level results]
Field Duplicates	Recommended	Not specified
Continuing Calibration Verification (CCV)	At least every 12 hours (max 20 samples), and at end of each batch.	80-120% recovery for mid-level standards (70-130% for asterisked and non-listed analytes – see analyte table)
If DQOs are not met, repeat testing or report qualified test results. DQOs do not apply to RM DQOs if targets are < 10x MDL (derive lab-specific DQOs in this case) or to MS results where sample background exceeds spike amount.		

Internal Standards: Recommended internal standards include deuterium-labeled VOCs, fluorinated VOCs, and brominated VOCs.

Surrogates: Appropriate Surrogate Compounds must be added to each sample prior to extraction. Recommended surrogates include deuterium-labeled VOCs, fluorinated VOCs, and brominated VOCs (must differ from internal standards).

Calibration Verification Standard (CVS): Analysis of a second source VOC standard to ensure validity (accuracy) of the calibration. All calibrated and reported parameters must be included.

Continuing Calibration Verification (CCV): Calibration standards (typically a mid-point standard) must be re-analyzed periodically throughout the instrument run to monitor calibration drift. Run a CCV at least every 12 hours (maximum 20 samples), and at the

end of each batch.

Method Blank: A clean solid matrix (or methanol and reagents only) that is processed through the entire extraction and analysis process in the same manner as a sample. Analyze an aliquot of methanol extract equivalent to the default sample amount.

Lab Control Sample: A clean solid matrix (e.g. oven baked sand) that is spiked and processed through the entire extraction and analysis process in the same manner as a sample. Analyze an aliquot of methanol extract equivalent to the default sample amount. All calibrated and reported parameters must be included. This spike provides a means to assess for the accuracy of the extraction procedure and performance of the analytical system in the presence of methanol.

Matrix Spike Sample: Analysis of a second aliquot of an equal amount of methanol extract that is taken from the same vial and spiked prior to analysis. It is recommended to spike with the same standard used for the LCS at a concentration that is slightly less than or equal to the mid-point of the calibration. Used for assessing sample matrix effects.

Lab Duplicates: Analysis of a second aliquot of an equal amount of methanol extract that is taken from the same vial to assess laboratory variability.

Field Duplicates: Recommended to assess sampling variability (precision). Frequency as per sampling plan.

Travel Blank or Field Blank (Field Methanol Technique only): Strongly Recommended. Travel Blanks and/or Field Blanks are necessary 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.

Prescribed Elements

The following components of this method are mandatory:

1. Samples must be either preserved in the field with methanol or collected using hermetically sealed sampling devices. Results must otherwise be qualified.
2. Methanol extraction is required with minimum 1.5 mL to 1 g ratio of methanol volume to wet weight of solids extracted.
3. Field methanol preserved samples must be physically agitated using a mechanical shaker for at least 15 minutes. Hermetic samples that are methanol extracted in the laboratory must be physically agitated using a mechanical shaker for at least 30 minutes.
4. When using GC/MS, at least two surrogates are required to be added to all samples prior to analysis. Stated calibration and internal standard requirements must be met. Initial GC/MS calibrations must be five points or more (no more than one point may be excluded).
5. Wherever possible, the same sample extract must be used for the analysis of both VHs6-10 and targeted VOC compounds, so that sub-sampling variability does not affect the calculated VPH result.
6. All target compound analysis must be conducted by GC/MS, except that BTEX, Styrene, and MTBE analysis may alternatively be conducted by GC-PID (Photoionization Detection). GC-PID is less selective than GC/MS, and is much more subject to false positives and false negatives than GC/MS.
7. Soil moisture content must be considered within data calculations for the total methanol extract volume for each sample.
8. Sample container materials, preservation, storage, and hold time requirements may not be modified. Samples analyzed beyond the stated holding time must be qualified. Refer to latest version of “BC MOE Sample Preservation and Hold Time

Requirements" for updates.

9. All stated Performance Requirements and Quality Control requirements must be met.

Apart from these limitations, and provided performance requirements are met, laboratories may introduce modifications to this method to improve quality or efficiency.

References

1. EPA 8260D, Test Methods for Evaluating Solid Wastes – Physical / Chemical Methods, SW-846, 3rd Edition, Method 8260D, Volatile Organic Compounds by Gas Chromatography / Mass Spectrometry (GC/MS), Revision 4, February 2017. United States Environmental Protection Agency, Washington, D.C.
2. EPA 5030C, Test Methods for Evaluating Solid Wastes – Physical/Chemical Methods, SW-846, Method 5030C, Purge and Trap for Aqueous Samples, Revision 3, May 2003. United States Environmental Protection Agency, Washington, D.C.
3. EPA 5035A, Test Methods for Evaluating Solid Wastes – Physical/Chemical Methods, SW-846, Method 5035A, Closed System Purge and Trap Extraction for Volatile Organics in Soil and Waste Samples, Revision 1, July 2002. United States Environmental Protection Agency, Washington, D.C.
4. EPA 5021A, Test Methods for Evaluating Solid Wastes – Physical/Chemical Methods, SW-846, Method 5021A, Volatile Organic Compounds in Soils and Other Solid Matrices using Equilibrium Headspace Analysis, Revision 2, July 2014. United States Environmental Protection Agency, Washington, D.C.
5. ASTM D6418-09, Standard Practice for Using the Disposable En Core Sampler for Sampling and Storing Soil for Volatile Organic Analysis.
6. EPA 8021B, Test Methods for Evaluating Solid Wastes – Physical/Chemical Methods, SW-846, Method 8021B, Aromatic and Halogenated Volatiles by Gas Chromatography using Photoionization and/or Electrolytic Conductivity Detectors, Revision 3, July 2014. United States Environmental Protection Agency, Washington, D.C.

Revision History

Sept 15, 2017	Significantly expanded list of analytes to cover volatile substances in 2017 CSR. Added reference to EPA 8021B for PID parameters and updated EPA 8260 and EPA 5021 reference methods. Updated QC and internal standard acceptance criteria to support broader list of VOC analytes. Matrix spike (or RM) added to QC requirements. Minimum methanol shake times were added to prescriptive elements (15 mins for field methanol preserved samples, 30 mins for hermetic samples).
Apr 9, 2014.	Draft version for review and comment by BCELTAC and stakeholders. 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. CVS frequency changed to once per initial calibration.
Oct 1, 2013	New method added to BC Lab Manual. Effective date for this method is October 1, 2013.