Volatile Organic Compounds in Solids – 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

In order 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).

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/MS. The sample may be focused onto a solid sorbent trap prior to being desorbed onto the GC column.

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 provided that all stated performance requirements and prescribed (mandatory) elements are met.

Parameter Applicability, MDLs

The analytes listed below represents only a partial list of compounds which may be analyzed by this method. Refer to EPA Method 8260C for a more complete list of applicable analytes. The MDLs listed below are achievable for this method 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.

Compound	Approx MDL (mg/kg)	EMS Code
benzene	0.01	B020 X384
bromodichloromethane	0.01	B012 X384
bromoform	0.01	B013 X384
carbon tetrachloride	0.01	defined on request
chlorobenzene	0.01	C010 X384
chloroform	0.01	C032 X384
dibromochloromethane	0.01	C033 X384
1,2-dichlorobenzene	0.01	defined on request
1,3-dichlorobenzene	0.01	defined on request
1,4-dichlorobenzene	0.01	defined on request
dichloromethane	0.20	M041 X384
1,1-dichloroethane	0.01	C021 X384
1,2-dichloroethane	0.01	C022 X384
1,1-dichloroethylene	0.01	C024 X384
1,2-dichloropropane	0.01	C025 X384
cis-1,2-dichloroethylene	0.01	defined on request
trans-1,2-dichloroethylene	0.01	defined on request
cis-1,3-dichloropropene	0.01	C027 X384
trans-1,3-dichloropropene	0.01	C028 X384
ethylbenzene	0.01	B021 X384
ortho/meta/para-xylenes	0.02	defined on request
methyl-tertiary butyl ether (MTBE)	0.05	defined on request

styrene	0.01	S010 X384
1,1,2,2-tetrachloroethane	0.01	C080 X384
tetrachloroethene	0.01	T030 X384
1,1,1-trichloroethane	0.01	T016 X384
1,1,2-trichloroethane	0.01	defined on request
trichloroethene	0.01	T029 X384
trichlorofluoromethane	0.05	T070 X384
toluene	0.05	T001 X384
vinyl chloride	0.05	defined on request

Where appropriate, the method may be used for other compounds not listed here, if performance requirements and Quality Control requirements can be met.

Matrix

Soil
Sediment
Other 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.

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.

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 regard 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 grams wet weight) is collected (typically with a disposable coring device) and extruded into a known volume of high purity methanol (typically 10.0 mL) contained in a pre-weighed vial. Two preserved sub-sample vials per sample are recommended as a precaution against leaks, breakage, or error.

ii) **Hermetic Sampler:** A representative sub-sample of soil (typically ~ 5 grams 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 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. 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 required for VOC/BTEX analysis. VH surrogates may be combined with surrogates required for VOC/BTEX analyses. 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 brief 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

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 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 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 amount of internal standards are 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 one Internal Standard is required for BTEX/Styrene/MTBE analysis. At least two Internal Standards must be used for the analysis of other multi-component VOC lists. Continuing calibrations may be employed while Calibration Verification Standards meet acceptance criteria for all reported compounds.

Raw results (i.e. ug/L or ug 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% for all listed and routinely reported parameters.

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 listed and 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: The laboratory's reported detection limit must be greater than their statistical Method Detection Limit (MDL). Where possible, MDLs should be 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	Within 50% of initial calibration or last CCV
Surrogates	All samples and QC	60-140% recovery
Calibration Verification Standard (CVS)	1 per initial calibration	80-120%
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)	VOCs with b.pt. ≤ 20°C and dichloropropenes: 60-140% recovery Other listed VOCs: 70-130% recovery
Lab Duplicates	1 per batch (max 20 samples)	≤ 40% RPD
Field Duplicates	Recommended	Not specified
Continuing Calibration Verification (CCV) (applicable to mid-level stds)	At least every 12 hours (max 20 samples), and at end of each batch.	VOCs with b.pt. ≤ 20°C and dichloropropenes: 70-130% Other listed VOCs: 80-120%

* Minimum DQOs apply to individual QC samples, not averages, at levels above 10x MDL. Report qualified data when DQOs are not met.

QC Details

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 the extraction or mechanical agitation process. Recommended surrogates include deuterium-labeled VOCs, fluorinated VOCs, and brominated VOCs (must differ from internal standards).

Calibration Verification Standard: 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 exactly 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 exactly 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.

Lab Duplicates: 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).

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

Travel Blank or Field Blank (Field Methanol Technique only): Travel Blanks and/or Field Blanks are strongly recommended 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:

a) Samples must be either preserved in the field with methanol or collected using hermetically sealed sampling devices. Results must otherwise be qualified.

b) Sample holding times must be adhered to. Samples extracted or analyzed beyond the stated holding time must be qualified.

c) Methanol extraction is required with minimum 1.5 mL to 1 gram ratio of methanol volume to wet weight of solids extracted. At least one surrogate is required to be added to all samples prior to extraction.

d) Wherever possible, the same sample extract must be used for the analysis of both VH_{s6-10} and targeted VOC compounds, so that sub-sampling variability does not affect the calculated VPH result.

e) 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.

f) Stated calibration and internal standard requirements must be met.

g) Samples that exceed the calibration range must be diluted and re-analyzed, or reported as estimated or minimum values.

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

i) 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 in order to improve quality or efficiency.

References

i) US EPA Method 8260C, Volatile Organic Compounds by Gas Chromatography / Mass Spectrometry (GC/MS), August 2006.

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

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

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

v) 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 : wet soil changed from 2:1 to 1.5:1. CVS frequency changed to once per initial calibration. DQOs modified (widened for gaseous VOCs and challenging compounds, surrogate DQOs widened to 60-140%). GC-PID added as option for BTEX/Styrene/MTBE. Number of internal standards required for BTEX/Styrene/MBTE reduced to one. Effective date for this revision is Nov 1, 2014.
Oct 1, 2013	New method added to BC Lab Manual. Effective date for the Oct 1, 2013 version of this method was November 15, 2013.